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The moisture content of acid soils as a factor influencing their lime requirement

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THE MOISTURE CONTENT OF ACID SOILS AS A FACTOR INFLUENCING THEIR LIME REQUIREMENT .

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THE MOISTURE CONTENT OF ACID SOILS AS A FACTOR INFLUENCING THEIR LIME REQUIREMENT.

The following work was planned to investigate the possibilities of changes of the lime requirement of acid soils when the moisture content of these soils is materially altered. Then, when changes were observed, a study of the relationships of the differences in the lime requirement, with those of the true acidity, expressed as hydrogen ion concentration, and those of the solubilities of the two soil elements, iron and aluminum, which seem to be partially responsible for this acidity, was conducted. Finally, an endeavor was made to correlate the variations in the crop-producing power of two of the soils with those produced in the above properties and constituents when the soils were air-dried previous to the planting of crops.

Investigations upon the subject of the work reported herein are of importance because observations in the field seem to indicate that changes in the moisture content of soils influence the concentration and reaction of the soil

solution to such an extent that the relative productivity of the soils is affected. These changes in moisture are apparently dependent upon weather conditions and upon tillage, irrigation, and drainage operations. Therefore, exact knowledge of the influences of the changes in the moisture content of soils seems essential for the intelligent treatment of the soil in order to produce an appreciable increase in the yield per acre of marketable crops.

Evidences of changes in the productivity of soils, subsequent to treatments in regard to moisture, have been observed frequently by practical horticulturalists, especially by those engaged in greenhouse and nursery practice. Soils are commonly stored in an air-dried condition. The crop-producing power of the soils is altered without a doubt. Then, the practice of destroying weed seeds, parasitic fungi, disease-producing organisms, and insects by the application to the soil of dry heat and steam, with or without pressure, is fast becoming a necessity in the establishments of commercial growers. For this reason, alone, exact knowledge of the influence exerted upon the properties of the soil by changes of moisture conditions are essential in order to reestablish a suitable environment for successful and profitable plant propagation.

Likewise, in soil investigation in the laboratory, very frequently little or no attention is paid to the changes a soil undergoes in regard to its moisture content between the time of collection from the field and the time

of analysis in the laboratory. Without a doubt, the soil must pass through a series of moisture alterations which materially influence the ultimate results of such an analysis. With these particular points in mind, the following data have been collected.

Review of Literature

Many investigators have observed that for some soils drying previous to planting is beneficial to crop production.

Ritter (33) by measuring the formation of the acid and the carbon dioxide in cultural solutions studied the bacterial activity of wet and dried soils, as affected by the physical and chemical properties of the soil, the character of the cultural medium, the kind of vegetation, alternate wetting and drying, and the temperature. He reported that drying soils hastened fermentation and intensified the production of acid. The kind of soil and the water content of the soil were factors which determined the amount of acid formed and the length of time required for its formation.

Lodge and Smith (24) found that they could obtain different results in regard to the development of bacteria after sterilizing soils rich in organic matter than they could from soils deficient in organic matter. Bacterial development was accelerated in decoctions from soils of the former group and retarded in those of the latter.

Rahn (32) observed that dry soils lose the greater

part of their intensified putrefactive power after they have been remoistened for twenty-four hours, and then they do not differ materially from the original moist soils. The bacterial changes go on more rapidly in dried soils remoistened -- 60% more rapidly in garden soil, 10 to 30% in ordinary farm soil, and inappreciably in light sandy soil. The rapidity of drying had little effect.

McMiller (27), performed an experiment upon the influence of gypsum on the solubility of potash in soils. He used soils which he had previously air-dried. He attributed his results to the fertilizer treatment and did not consider the influence that the air-drying had upon them. This is only one example of many such experiments.

Gedroits (11) reported his work which covered a period of six years in which he compared the fertility and productivity of soil in dry-air storage with that under natural conditions. A gradual increase, except for the fifth year of storage, in an oat crop grown without fertilizer with the length of storage was observed. With flax, where a complete fertilizer was used, there was a uniform increase during the four years after the first. As a check upon his work, he tested samples of all of the soils, collected and stored during the period, in one season. His former data was confirmed. He concluded that storing soil in an air-dry condition increases its productivity in proportion to the period of

storage, and also increased in a corresponding degree the percentage of phosphoric acid and nitrogen in the crops grown upon it.

Klein (22) concluded that previous drying increased nitrification in soils also, and that the maximum is reached after the third drying. The nitrates were likewise increased by increasing the organic content of the soil. He confirmed the works of Ritter and Rahn, cited above, in regard to the activity of bacteria up to the third drying of the soil, but he stated that thirty-five days instead of twenty-four hours were required for a soil to resume its normal condition after drying, and that its activity then was slightly greater than the original soil.

Klein also drew the following conclusions from his work: 1. Drying a soil previous to planting has a beneficial effect upon plant growth. 2. This beneficial effect, caused by a change in the water soluble matter, is dependent upon the organic matter in the soil. 3. Previous drying has no effect upon the total nitrogen in the dry matter of the crop. 4. Drying out of a soil has but little effect upon the availability of potassium, calcium, and phosphorus of the soil. These last two conclusions do not seem to be quite in accord with those of Rahn.

Temple (45), in his study with the nitrification of several nitrogenous fertilizers in "acid or non-basis" soils, concluded as follows: 1. Ammonia is formed in excess of the amount of acids produced when such organic

materials as tankage, dried blood, peptone, asparagin, etc., are acted upon by soil organisms. The ammonia satisfying the acids produced, allows the nitrifying organisms to funtion normally. 2. The acid fraction of the ammonium salts of the organic acids being used by the organisms for food is broken down so that ammonium carbonate is formed. 3. The relative nitrifying power of ammonium sulphate is increased as much by organic calcium salts as by calcium carbonate. 4. Organic compounds can be so decomposed by soil organism that they will form by-products which in turn can proceed. He obtained results from soil heated to 80^{o} C. results similar to those from fresh untreated soils.

Several observations of the effects of partial sterilization of soils by sunlight have been recorded. Russell (37) conducted an experiment at the Experiment Station, Wye, England. The experiment showed after ten days that sunlight could equal volatile antiseptics in removing the factor limiting productiveness in ordinary soils. The soil used consequently absorbed oxygen more readily than before. Howard and Howard (15) and Fletcher (10) while working in India found that soils dried in direct sunlight were increased in fertility. They practically confirm Russell's work.

Fletcher cited a common practice in the rice lands of the Bombay Presidency in India. The seed-bed for trans-

planted rice was subjected to a process known as "rab" in the vernacular of the country. A layer of branches, grass, cow-dung, etc., was spread over the surface of the plot, often a few meters square, selected as the site of the seed-bed. This material was then slowly burned just before the breaking of the monsoon. Cow-dung and straw were considered the best for this treatment.

He attributed the infertility of the soil to the presence of some toxic substance which may be rendered insoluble and innocuous by toluene. This property was also removed from extracts of soil by heat. His conclusion was that a much lower temperature would produce the same results, and that the fertilizing effect of the sunlight is able to decompose this detrimental substance.

Russell and Hutchinson (38) disputed this hypothesis and claim that Fletcher's toxin, if it had been present, should have shown a depression at once after drying which it did not, and it should be proportional to the amount of toxin in some untreated soil added to the experiment.

They based the injurious factor upon a biological hypothesis. There are organisms in the soil prohibiting the development of bacteria which are essential to plant growth. These organisms are widely distributed and constitute an important factor in the fertility of soils.

The age of the custom of utilizing the beneficial effect upon the soil, rendered by sunlight as an agent, is indicated by King (21) when he tells of the Chinese making

"kangs" of clay subsoil, and after thoroughly drying them, tearing them apart and using them for fertilizer.

Sullivan and Reid (44) stated that the power of air-dried soils to decompose hydrogen peroxide persists for years. Heating soils in dry heat at 105°C had little depressing action, but heating under 10 atmospheres of pressure in an autoclave retards this catalytic power. They found, further, that various inorganic substances and several organic compounds when in a state of partial oxidation had the power of decomposing hydrogen peroxide, while several other organic compounds also increased the catalytic power of manganese dioxide. In general, the catalytic power possessed by soils seemed to them to be due "not to an enzyme such as catalase, but rather to the inorganic and organic matter working separately, conjointly, or in an activating combination." A strong catalytic power in a soil seemed to give to them "a priori evidence" that the many factors making for soil fertility would be prominent, and that the soil would possess productivity.

Peterson (31) showed that although a large increase in the solubility of soil phosphorus was obtainable by heat alone, special conditions were necessary. Heating subsoils considerably over 100°C, after oxidation, produced a marked effect upon the solubility of the phosphorus present, while a decrease in one case and two small increases were noticeable subsequent to the oxidation of the surface soils. He found also that the soluble iron and alum-

inum increased "roughly parallel to the increase in the soluble phosphorus but not strictly proportional to it." He attributed this occurrence to two conditions: 1. The iron and the phosphorus may be combined with the carbon, or 2. They may be combined with each other and not with the carbon. Manganese remained constant in solubility.

Robinson and McCaughey (34) state that, on being heated in the air, practically all soils become red. This appeared to show that the film of ferruginous material coating the soils particles is dehydrated and converted more or less completely into ferric oxide. Heating the soils in a stream of hydrogen causes them to turn gray and metallic iron can be detected. According to these authors these facts indicate that all soils, save white sand, have a coating of this ferruginous material, and moreover, that it is more or less mixed with organic matter. A yellow color produced with some soils may be the result of a thinner film over the particle.

Kelley and McGeorge (20) in their studies with Hawaiian soils state that burning soils at moderate temperatures greatly increased the solubility of aluminum and potassium as well as greatly improving the physical conditions of the soils and successfully destroying weed seeds, parasitic fungi, disease-producing organisms, and insects. At higher temperatures, especially with the aid of oxidizing conditions, a wasteful destruction of soil organic matter and a decrease in the solubility of the aluminum and

potassium set in.

A condition toxic to germination and the subsequent growth of plants, usually of short duration, followed steam sterilization of soil under pressure.

They reported increased water solubility of phosphorus with increased heat and time of extraction. Manganese followed the same course. Conflicting results were obtained upon the solubility of iron oxide and aluminum in air-dried and oven-dried soils, but there was an apparent increase in the solubilities of both with the time of extraction. Potash was much more soluble in air-dried and fresh soils than in oven-dried soils.

These two investigators concluded that the most important set of factors concerned in effecting the solubility of inorganic soil constituents was of a physical nature, that these factors act through the soil moisture in its relation to the physical properties of the soil. The most particular action of heat was to evaporate the water films surrounding the particles which held the soluble matter under high pressure. The soluble constituents were left deposited upon the surfaces of the particles in a condition to be more readily taken up when water was again added. Heating may also improve aeration.

Noyes (30), while making a study of the Veitch Method (48) for the determination of the lime requirement of soils, collected at different depths, samples of a silty clay loam underlain by limestone; and after air-drying them

and crushing them so that all except the stony material passed a one millimeter sieve, he treated the soils according to prescribed directions except for the first step. With the first portion he used no limewater, with the second he used no limewater and did not evaporate it upon the steam bath. Hopkin's Potassium Nitrate Method (16) was used as a check. He observed that reactions between the soil, the water, and the calcium hydroxide at the steam bath temperature did not represent the lime requirement of the soil at the ordinary temperature.

Beaumont (5), in studying the reversibility of the colloidal condition of soils under a series of treatments in which there was occasion to use various degrees of heat and moisture, observed that if a soil was allowed to stand with an excess of moisture a colloidal material resembling ferric oxide was obtained. To confirm his idea that this colloidal material, in part at least, was ferric hydrate, he conducted an experiment with moist, air-dried, oven-dried, and sterile oven-dried soils standing in 200 percent of water. The soils were shaken with approximately N/30 hydrochloric acid, allowed to stand for a while, and then filtered. Iron was determined in the filtrate colorimetrically. Oven-drying previous to standing in water caused an increase in the amount of easily soluble iron in the soils, while the previous sterilization inhibited the formation of these easily soluble compounds. He attributed the results to the bacterial destruction of the organic matter in the unsterile

soil. These iron compounds may be brought into solution and hydrolyze to form colloidal ferric iron.

Truog (46) stated that when conditions were properly controlled the reactions due to soil acidity occur according to chemical equivalence and exhibit all the properties of true chemical reactions. In most upland soils such substances as kaolinite and other acid silicates are responsible for most of the acidity. Soils high in organic matter may likewise be high in organic acids. These acid substances may exist in either of two conditions, the crystalloidal or the colloidal; and their acid reaction is due to their chemical nature and not their condition.

Conner (8) confirms Truog as to the materials which cause acidity. Portions of five samples of soils of different types were kept in air-dry, one-fourth saturated, one-half saturated, and fully saturated conditions. Acidity was tested in the moist and air-dried condition. Potassium-nitrate extracts of the soils were analyzed. With soils low in organic matter the highest degree of acidity was noted with the one-half saturated samples, while with those high in organic matter the fully saturated possessed the most. When the moist soil was taken at the close of the experiment and air-dried, the one-half and one-fourth saturated samples showed inconsistent changes in acidity, while the fully saturated showed a decrease.

In the analysis of the extracts, calcium, magnesium, and silica showed variations in solubility due to different

moisture conditions, but the variations were more striking with iron, manganese, and aluminum. The largest amount of iron was found in the fully saturated samples and supposedly in the ferrous state, because upon drying the soils this iron was made insoluble. Much more soluble manganese was also found in these samples, but drying did not render it insoluble. The amount of soluble aluminum was less in the fully saturated mineral soils, but conflicting results were noted with those high in organic material.

In another paper (7), Conner drew the following conclusions: 1. The acidity of aluminum silicates is not only in proportion to the ratio of AL_2O_3 to SiO_2 but also in proportion to the water of constitution. 2. The greater the proportion of water in the silicate the more acid is the reaction. 3. Heating and the consequent driving off of the water of constitution in these aluminum silicates lowers the acidity until all of the water is removed when neutrality is reached. 4. Ignition of acid soil also destroys the acidity.

Walker (49), in an investigation similar to Conner's, confined his study to that of a black muck. He compared it in the original, air-dried, aerobic, anaerobic, lime plus aerobic, and lime plus anaerobic conditions. His conclusions were, ~~that~~ 1. The air-drying increased the lime requirement. 2. If the soil was frequently stirred for a period of eight months, while moist, it showed a decidedly less increase in acidity than when it was kept covered

with water in a sealed jar. 3. With the soil first neutralized with calcium oxide and kept for a period of eight months, under either aerobic or anaerobic conditions, a great deal more acidity than with the unneutralized soil under identical conditions was developed. This occurrence he explains by the Law of Mass Action. 4. All samples stored in a moist condition increased in lime requirement, but the air-dried sample decreased in acidity during storage for eight months.

Sharp and Hoagland (42) attributed soil acidity to an excess of hydrogen ions in the soil and proceeded to prove it by using the hydrogen electrode apparatus. The soils were suspended in water. Air-dried soils which had been passed through a one millimeter sieve gave rise to acid solutions. The solutions, in other words, contained a predominence a H-ions over OH-ions.

Soils which had been previously heated in a muffle furnace just below red heat, or blasted, showed a decrease in the intensity of their acidity. A soil heated to $140^{\circ}C$, although the data are meager,gave an indication that the hydrogen-ion concentration may have been slightly increased.

Konig, Hasenbaumer, and Glenk (23) also presented an electrical method for the determination of the changes which soils undergo when heated and when air-dried. Their results, obtained by reading electrolytic conductivities of the soils in question, indicated to them that the

ordinary drying out of soils produced a partial suspension of the colloidal conditions and hence an increase in the solubility of the plant food which existed in a colloidal combination.

Schreiner and Lathrop (40) made the general statement that, after they have been sterilized, soils possess some substance which is decidedly injurious both to the germinating and growing plant, particularly if an excess of calcium carbonate is not present while the soils are being heated to prevent the formation of acids. After standing the injurious effect is lost, especially when the soil is planted. Schreiner and other workers in the Bureau of Soils of the United States Department of Agriculture (41) attributed this injurious effect to the presence of detrimental organic decomposition products such as dihydroxystearic acid, picoline carboxylic acid, and aldehydes, in addition to some of the inorganic soil constituents.

Additional information upon this subject has been gathered by Ruprecht and Morse (35 & 36) who showed positive proof of the presence and injurious effect of salts of aluminum, iron, and manganese upon seedlings, and also by Abbott, Conner, and Smalley (2), Ames, Boltz, and Schollenberger (3 & 4), Hartwell and his coworkers (12, 13, & 14,), Kelley (19), Miyake (28), and Ewell (29) for the inorganic soil constituents.

Summary of Literature Reviewed

The following points may be drawn from the foregoing literature:

1. The original moisture contents of the soils used were various.

2. The methods used for the determination of the lime requirements of the soils were numerous. The reader is respectfully referred to the works of MacIntire (26), Stephenson (43), Noyes (30), and Veitch (48) for a study of the merits and comparison of methods used.

3. No uniform method of extraction of the soils analyzed was practiced. Some were water extractions, while others were acid or salt extractions.

4. The effect of heating and air-drying upon the acidity of the soils in the majority of cases was only a subordinate object of research.

5. The results of moisture changes were not all concordant. This can be expected since the conditions under which the investigations were carried on differed.

6. The general opinion is that soils high in organic matter, or those to which much organic matter is added, possess greater acidity than the soils which are largely mineral in nature, and that the acidity of the former is increased by either air-drying or oven-drying, while the performance of the latter is uncertain.

7. Ignition greatly reduces the lime requirement of any soil.

8. The length of time that acidity, or a change in acidity, persists in a soil altered by drying and kept in various conditions of storage is questionable.

9. The crop-producing power of soils stored in an air-dried condition for a long period of time is increased.

10. Sunlight produced a beneficial effect upon soils.

11. The injurious factor in soils may be the result of physical, chemical, or biological agencies influencing the soil solution.

12. Almost,all of the writers agree that iron, aluminum, manganese, and silicon are, when they occur in certain compounds, responsible for much of the inorganic acidity; and that substances derived from the decomposition products of the soil organic matter, the disintegration of which is dependent upon the moisture content of the soil, add their influence.

13. Physical changes, especially in the colloidal material held in the film surrounding the soil particles, are contributed also as an explanation of the results obtained before and after drying a soil.

14. Biological changes appear to proceed more rapidly after the soil is dried and again remoistened than when it is left untreated; and such increased activity, which is dependent upon the type of soil and its moisture content, results in the accumulation of more soluble matter in the soil solution.

Problems Involved

A review of the previous literature opened up the following problems for consideration:

1. The choice of a satisfactory and convenient method of storing soils which would prevent changes in their moisture condition during a period of investigation.

2. The selection of soils in regard to their texture, organic content, reaction (acid, neutral, or alkaline), original moisture condition, previous treatment, and relative productivity for a study of the effects produced by moisture changes.

3. The formulation of a workable and rather extensive plan of soil treatment, to include drying at different degrees of temperature and remoistening with various amounts of water, in order to produce uniform alterations of moisture under controlled conditions.

4. The detection of differences in the lime requirements of soils, if any are produced, when the moisture content of soils is altered.

5. The adoption of a satisfactory method, where no heat is necessary, for the determination of the lime requirement of soils under any moisture condition and sensitive enough to detect differences in lime requirement resulting from relatively small moisture changes.

6. The comparison of the lime requirement with the true

acidity of soils, expressed as hydrogen ion concentration.

7. The adoption of a suitable method for the determination of the hydrogen ion concentration of soils sensitive enough to detect the small differences subsequent to changes in the moisture content of soils.

8. The correlation of changes produced in the organic and mineral constituents of soils with those produced in the lime requirement and hydrogen ion concentration.

9. The adoption of adequate methods for the determination of constituents of soils sensitive enough to detect the differences produced subsequent to alterations of the moisture condition of soils.

10. The correlation of alterations produced by changes in moisture content, of lime requirement, hydrogen ion concentration, and organic and inorganic contents with those of the crop-producing power of soils.

Treatment of Problems Involved

The above problems were treated as follows:

1. The storing of soils in stoppered wide-mouthed bottles proved to be the most satisfactory and convenient method to prevent loss of moisture.

2. Three surface soils were selected. These soils represent three acid soils which have been subjected to widely different conditions. Soil No.I represents that group of soils which have become acid, partially at least,

due to cultivation and the application of commercial fertilizers. Soil No. II is a sample of freshly cleared soil which is rather poorly drained and high in its organic constituents. Soil No. III is a representative of unproductive acid soils which as a whole have not been under cultivation recently, although their drainage conditions are fair.

Their mechanical analyses, according to the centrifugal method of the United States Bureau of Soils, (9), are as follows:

Table I

Mechanical analyses of soils used in experimental work. (Expressed in percentages by weight, oven-dry basis)

Name of separate	Size mm.	Soil No. I	No. II	No. III
Fine gravel	2-1	0.99	1.32	4.99
Coarse sand	1-0.5	1.50	3.39	4.44
Medium sand	0.50-0.25	1.85	2.42	2.96
Fine sand	0.25-0.10	15.75	11.16	3.76
Very fine sand	0.10-0.05	53.26	54.52	6.06
Silt	0.05-0.005	20.36	20.78	48.92
Clay	0.005- .--	6.29	6.41	28.87

Further information regarding the properties of these soils is found in Table II.

Table II

Characteristics of soils used in experimental work.

	Soil No.I	Soil No.II	Soil No.III
Classification	Fine Sandy Loam	Fine Sandy Loam	Silt Loam
Color (air-dried)	Light brown	Dark gray	Light brown
Color (after ignition)	Reddish yellow	Cream	Reddish yellow
Loss on ignition	6.55%	11.57%	9.25%
Action towards litmus	All turned blue paper red immediately		
Lime requirements:			
Truog's zinc sulfine method (46)	More than medium acid	Nearly strong acid	About medium acid
Jones' calcium acetate method (18)	1.87 tons per acre 2,000,000 pounds	3.60 tons per acre 2,000,000 pounds	1.58 tons per acre 2,000,000 pounds

Note: 2,000,000 pounds is the approximate weight of the first seven inches of soil in one acre. The expression "per acre 2,000,000 pounds" is a short and convenient way of conveying this idea.

Previous treatment of soils used in experiment

Soil No,I was collected from one of the oldest fields on the farm of the Massachusetts Agricultural Experiment

Station at Amherst. A record of this field has been kept for thirty-eight consecutive years, and in this time it has received only commercial fertilizers (35 & 36). Since 1890 the particular plot (Field A. Plot 6) from which the soil was taken has received annually the following application of chemicals:

45 pounds of nitrogen per acre in ammonium sulphate.

80 pounds of phosphoric acid per acre in dissolved bone black.

125 pounds of potash per acre in muriate of potash.

Lime at the rate of 1 ton per acre was applied in 1898 and again in 1905.

The stubble and catch crops were plowed under and have been the only source of organic matter.

The crop grown the season previous to sampling the soil was corn. A seeding mixture of clover and grasses had been sown in the standing corn. Even the red top in the mixture was affected by the toxic property of the soil.

The type designation of this soil is Merrimac fine sandy loam.

Soil No.II was collected from a newly cleared area which had just been plowed for the first time. Only the soil from the poorly drained places over an area of one-half an acre was selected. This area is about 150 yards east of the sheep barn on the Massachusetts Agricultural College Farm. A thicket of brush and sedges covered the area for a number of years previous to clearing. The type desig-

nation of this soil is Hartford fine sandy loam.

Soil No. III was collected from Eagle Hill, also known as Hungerford Hill, Ithaca, N.Y. The elevation of this hill is 1200 feet. The soil is a representative sample of the distinctive type of Volusia silt loam. It is a glaciated soil underlaid with shale and sandstone. A large number of fragments from these rock formations were present in the soil. Where the samples were collected, vegetation was rather limited to a few plants, i.e., cinquefoil, paint-brush, danthonia, etc. None save the natural vegetation has covered the area for the last twenty years.

3. Table III contains an outline of the plan of treatment used in the investigation with the above soils.

Table III

Plan of soil treatment for a study of the effects of altered moisture conditions.

Treatments

I. Soil in untreated field moisture condition.

II. Soil air-dried in greenhouse at 20°C to 22°C

III. Soil oven-dried at 100°C to 105°C for twenty-four hours.

IV. Soil ignited in silica dishes.

Sub-Treatments

I. Soil with no water added.

II. Soil with 25% water added (oven-dry basis, by weight).

III, Soil with 50% water added.

IV. Soil with 100% water added.

Duplicate samples for each sub-treatment were made up. They were put in stoppered eight-ounce glass bottles and the bottles were placed on a bench in the laboratory where the temperature was fairly constant. No moisture was added throughout the whole experiment after the initial application had been made, and then only freshly distilled water was added.

4. Part I of this paper includes the data collected showing the changes in the lime requirement of Soil No.I and Soil No.II when determinations were made upon a series of samples of these two soils which were treated according to the above plan after a modification of Jones' calcium acetate method (18) for the determination of lime requirement had been adopted.

5. Part II includes a repetition of the procedure of Part I; the treatment of a third soil, Soil No.III, by the same plan; data showing the influence of moisture upon the hydrogen ion concentration and water extractable-iron and aluminum content of all three of these soils, besides the methods used for detecting differences in them; and the results drawn from a study of the relationships of these soil properties and constituents to each other.

Only two inorganic constituents were studied in these relationships because of numerous limitations, one of which was the dearth of adequate methods sensitive enough for the detection of small changes produced in the limited amounts of extractable substance available.

6. Part III records an attempt to correlate the changes, produced by air-drying samples of Soil No.I and Soil No.II of lime requirement, hydrogen ion concentration, and water-extractable iron and aluminum content with those of the crop-producing power of these two acid soils. Three crops possessing different sensitivities towards soil acidity were selected for this particular problem.

PART I

THE RELATIONSHIP OF MOISTURE TO THE LIME REQUIREMENT OF ACID SOILS.

The first part of this investigation involved a study of the relationship of moisture to the lime requirement of soils. An attempt was made to determine the difference in lime requirement, if any existed, between samples of the soils taken directly from the field, untreated as regards moisture, and other samples of the same soils which were first subjected to either (a) air-drying, (b) oven-drying, or (3) ignition; and also between samples similarly treated when variable amounts of moisture were added to each and then kept at constant moisture content. The effect of the length of time that the samples were subjected to given moisture conditions was also studied.

Preparation and Treatment of Soils for Experiment.

On November 18, 1919, the sample designated as Soil No. I was collected from the field. A composite sample of the surface soil where no crop existed was taken. The soil was immediately taken to the laboratory in sacks, thoroughly mixed, and passed through a one-quarter inch mesh sieve. One-half of the soil was then placed in

tared jars and kept at constant weight. The other one-half was taken directly to the greenhouse where the temperature was 20°C to 22°C and spread out upon heavy wrapping paper to the depth of one-half to three-quarters of an inch. Since the weather at the time was exceedingly cloudy, the soil was allowed to remain in the greenhouse about a month. It was rolled with a wooden rolling-pin and mixed occasionally to insure thoroughness of drying before it was used for experimental purposes. The resulting air-dried soil was also placed in jars and covered until it could be used for further investigation.

On November 21, the sample designated as Soil No.II was collected. It was likewise taken to the laboratory. Since it was frozen solid, it was heaped upon the floor of the unheated soil room and covered with sacks. Just as soon as it was thawed out it was thoroughly mixed and treated in the same manner as Soil No.I above.

Only Soil No.I and Soil No.II were used at this time. The plan outlined in Table III was followed in the preparation of soil treatments, and the investigation was continued for twelve weeks.

Determinations were made upon representative samples of the soils before the procedure for the sub-treatments was carried out. These determinations represent the initial lime requirements of the soils. Sub-treatment I served as a check upon subsequent ones.

The first determination showing the influence of the

addition of moisture was taken three weeks after the water was added. A second was taken at the end of six weeks, and a third at the end of twelve weeks. Such an arrangement allowed a good opportunity to study the changes, if any were produced, in the lime requirements of treated samples of the same soil under controlled moisture conditions for various periods of time, each of which was double that of the period just preceding it.

Method for the Determination of the Lime Requirement of Soils.

The method employed is a modification of the calcium acetate method described by Jones (18). A calcium acetate extract of the soil is made. The amount of acid present is then determined by titration, using sodium hydroxide as an alkali and phenolphthalein as an indicator.

Reagents required.

1. Calcium Acetate Solution - Dissolve 150 grams of chemically pure calcium acetate in 1500 cc. of freshly distilled water. To prevent the growth of molds, etc, add a few drops of formaldehyde.

2. Standard Sodium Hydroxide Solution - Prepare a one-hundredth normal solution of sodium hydroxide. Take precautions against the entrance of carbon dioxide.

3. Phenolphthalein - One gram of pure phenolphthalein is dissolved in 100cc. of 95% ethyl alcohol.

Analytical process.

5.6 grams of soil on the oven-dry basis is weighed out on a tared watch-glass. The soil is then thoroughly washed from the watch-glass, with the aid of a smooth funnel into a graduated shaker-bottle. Dilution of the soil-extract to a volume of 200 cc. is made after adding 5 cc. of calcium acetate solution. (5cc. is equivalent to 0.5 grams of calcium acetate). The rubber-stoppered shaker-bottle is then placed upon a shaker and allowed to remain there for exactly one hour.* The extract is filtered through a dry filter, the first 10-15cc. being discarded. Duplicate aliquots of 50 cc. of this clear soil-extract, immediately after thorough stirring, are taken for titration with N/100 NaOH, using 2 drops of phenolphthalein as an indicator. If they disagree they can be checked with a third aliquot.

The difference between the burette readings multiplied by 4 gives the amount of N/100 alkali necessary to neutralize the acidity in 200 cc. of the acetic acid extract. This figure times the factor, $\frac{1.8 \times 1000}{10}$, equals the number of pounds of lime (CaO required per 2,000,000 pounds of soil. (1.8 which represents the factor obtained by

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* The ideas of using the calcium acetate in solution and the shaking process for these determinations were obtained from Mr. F. C. Merkle, then an instructor in the Department of Agronomy.

Jones on a number of samples of Rhode Island, Massachusetts, Vermont, and New Jersey soils was retained although the conditions of extraction were somewhat altered).

By simplification, the result obtained by titration multiplied directly by 720, or 0.36, which are the factors on the pound and ton basis, respectively, gives the amount of lime (CaO) required per 2,000,000 pounds of soil, (approximately one acre - 7 inches.)

Remarks.

After considering a number of methods for the determination of the lime-requirement of soils to meet the conditions of the investigation the above method was worked out.

With the unmodified method of Jones it was found rather difficult to get duplicate samples of the same soil to agree in the amount of lime required. By experimenting with samples of oven-dried soils placed in shaker-bottles with the dilute calcium acetate solution and then shaken at the rate of about 120 shakes a minute, the data expressed in Table IV. were obtained. These are average results of duplicate samples. The results of the duplicates agreed in nearly every instance. Only in one instance did the difference amount to more than 1cc. of N/100 NaOH, which is equivalent to 0.36 ton or 720 pounds of lime. These results were confirmed later in the actual experiment.

Table IV

Effect of the time of shaking a soil in solution upon its lime requirement.

(Expressed in tons of CaO per acre, 2,000,000 pounds)

Time in minutes	10	20	30	40	60	90	120	180
Soil No.I	1.84	1.94	1.98	2.05	2.09	2.12	2.12	2.16
Soil No.II	2.63	2.92	3.02	3.06	3.28	3.31	3.35	3.38

These data show that by continuing to shake a soil in solution a slight rise in the lime-requirement of the soil as determined by subsequent operations is obtainable. The amount of increase lessens with the length of time, and the greatest increase comes before the end of sixty minutes. An increase of 0.25 ton against 0.32 ton of lime for Soil No.I and of 0.65 against 0.75 is noted for Soil No.II when the increase at 60 minutes is compared with the increase at 180 minutes.

The soil on the filter after the solution had been removed from it showed that, at the end of 60 minutes, the soil had become practically deflocculated. The resulting increase of the surface area of the soil exposed to the action of the calcium acetate solution might therefore account for part of the large increase, at least, in the lime-requirement.

The prepared samples of soils in the bottles were thoroughly mixed immediately before they were sampled. Those soils which were low in their moisture content were easily mixed and sampled with a small spatula; but with those which had high moisture contents it was necessary to use a piece of glass tubing as a pipette. In the latter instance, care was taken to see that each portion taken from the bottle was a representative sample of the soil suspension.

Tables V and VI give the resulting lime-requirements

Table V

Lime-requirements of Soil No.I at various moisture contents during a period of twelve weeks.

(Expressed in tons of CaO per acre 2,000,000 pounds)

Untreated

Moisture	34.9%	#59.9%	*84.8%	*134.9%
At beginning	2.11	2.11	2.11	2.11
End of 3rd week	2.05	2.10	1.95	1.99
" " 6th "	2.07	1.96	1.78	2.02
" " 12th "	1.98	1.80	1.93	1.90

Air-Dried

Moisture	2.7%	27.7%	*52.7%	*102.7%
At beginning	2.04	2.04	2.04	2.04
End of 3rd week	2.10	2.06	1.64	1.68
" " 6th "	2.10	2.34	1.64	1.70
" " 12th "	1.35	1.85	1.83	1.88

Oven-Dried

Moisture	0%	25%	*50%	*100%
At beginning	2.70	2.70	2.70	2.70
End of 3rd week	2.39	1.67	1.66	1.65
" " 6th "	2.29	1.60	1.67	1.86
" " 12th "	2.10	1.37	1.54	1.75

Ignited

Moisture	0%	#25%	*50%	*100%
At beginning	0.73	0.73	0.73	0.73
End of 3rd week	0.70	0.53	0.32	0.40
" " 6th "	0.39	0.55	0.32	0.42
" " 12th "	0.58	0.40	0.36	0.34

Table VI

Lime-requirements of Soil No. II at various moisture contents during a period of twelve weeks.

(Expressed in tons of CaO per acre 2,000,000 pounds)

Untreated

Moisture	61.4%	.86.4%	#111.4%	*161.4%
At beginning	3.12	3.12	3.12	3.12
End of 3rd week	3.25	3.41	3.06	2.90
" " 6th "	3.04	2.93	2.94	3.10
" " 12th "	2.87	2.77	2.78	3.47

Air-Dried

Moisture	2.7%	27.7%	52.7%	*102.7%
At beginning	3.33	3.33	3.33	3.33
End of 3rd week	3.14	2.71	2.70	3.01
" " 6th "	3.17	3.08	2.70	3.18
" " 12th "	2.90	2.75	3.30	3.18

Oven-Dried

Moisture	0%	25%	50%	*100%
At beginning	3.83	3.83	3.83	3.83
End of 3rd week	3.72	2.23	2.59	3.13
" " 6th "	3.49	2.43	2.47	3.19
" " 12th "	3.37	2.35	2.19	3.26

Ignited

Moisture	0%	25%	50%	*100%
At beginning	0.25	0.25	0.25	0.25
End of 3rd week	0.32	0.29	0.32	0.32
" " 6th "	0.27	0.26	0.31	0.25
" " 12th "	0.20	0.27	0.23	0.23

of Soils Nos. I and II which were subjected to various treatments and sub-treatments in regard to their moisture content over a period of twelve weeks. The figures represent the averages of duplicate samples of each sub-treatment.

In these and in subsequent tables, a mark preceding a number representing the percentage of moisture in a soil sample indicates the physical condition of that sample resulting from the presence of that particular percentage of moisture. The mark # signifies a puddled condition, whereas the mark * indicates that the sample was covered by water which varied from one-fourth to one inch in depth. The absence of any mark before a moisture percentage suggests that the soil is not wet enough to become puddled when stirred or else it is friable.

By the end of the first three weeks of the experiment a blue-green mold had accumulated upon the surface of the oven-dried samples of Soil No.II where 25% and 50% of moisture had been added. The same characteristic growth was observed where 25% moisture had been added to the oven-dried sample of Soil No.I.

A strong odor of putrefaction was noticeable where-ever the moisture percentage of the untreated, air-dried and oven-dried samples of both soils was sufficient to cause standing water to be present above the surface of the soil in the bottle. Samples of Soil No.II which contained more organic matter than Soil No.I possessed the stronger odor.

After the soils had been thoroughly stirred and sampled for the lime-requirement determinations at the end of the first three weeks and then allowed to settle again, a reddish-brown coloration of the solution was noticed. This coloration was not present at the beginning of the experiment. As time went on, the solutions became cloudy, more especially just under the surface of the standing water. A thin, white, translucent scum developed upon the surface of the water even upon the surface of the ignited samples. Upon this scum, except with those samples which had been previously ignited, blue-green and white molds, similar to those which appeared upon the oven-dried samples containing less moisture, developed. The most profuse growth was observed on the oven-dried soil samples which were subjected to the addition of 100% moisture. The depth of the water flooding these samples was about one inch.

Conclusions from Tables V and VI.

The results of the experiment show that a change in the moisture content of acid soils caused a change in their lime-requirements where the soils were stored under the conditions stated above. This change apparently varied somewhat with the type of soil. By reducing the moisture content of Soil No.I by air-drying, a decrease in lime-requirement resulted, while the reverse was true with Soil No.II. The increase was about 0.2 ton in the latter soil against a decrease of 0.07 in the former. An un-

questionable increase was produced in the lime-requirements of both soils after moisture reduction had been accomplished by oven-drying, but ignition caused a decrease to a fraction of a ton of lime. The relatively high reading of the ignited sample of Soil No.I may be due to insufficient ignition although the soils were ignited until no evidences of carbon black were discernible. Also, the greater loss on ignition of No.II would account for some of this difference, since the calculations were made on the oven-dry basis.

Further examination of the tables reveals not only changes in the lime-requirements due to the different treatments, which caused a reduction of the amount of moisture and of the organic matter present, but also changes due to the series of sub-treatments to which they were afterwards subjected. The difference in soil type altered the results as well as the length of time that the soil was subjected to the various treatments and sub-treatments.

Considering first the changes which took place in the untreated, air-dried, oven-dried, and ignited samples where no water was again added, it was observed that the general tendency of the lime-requirement is downward, i.e., as time went on, the lime-requirements of all such treated soil samples became less. The results were in every instance less at the end of twelve weeks than they were at the beginning. At first it was thought that the possible deterioration of the calcium acetate in solution might account for such results; but, by titrating some of the solution at the

beginning and again at the end of the period, no apparent change was noticeable.

With the untreated samples of the soils, representing the field moisture condition which had not been altered, very little change took place during the twelve-weeks period. A gradual change to less acidity occurred in Soil No.I; but in Soil No.II, a slight rise with 2 out of 4 treatments appeared at the end of three weeks before the gradual decline in acidity took place. The air-dried samples were probably altered to about the same lime-requirement as that of the original untreated sample soon after the experiment began and continued to remain at that level until after the end of the sixth week before a reduction occured. The reduction was also gradual in the oven-dried and ignited samples, except for the ignited samples at the end of the sixth week in Soil No.I, and the end of the third week in Soil No.II.

Sub-treating the four treated samples of each soil by adding 25% of moisture in the form of distilled water on the moisture-free basis by weight of the soil caused a depression in the acidity in almost all cases by the end of the third week. With the untreated, air-dried, and ignited samples of Soil No.I the changes were immaterial, but with the oven-dried sample there was a drop of over a ton, and the result obtained was much less than the lime-requirement of the original untreated sample when it was taken in from the field. A very similar performance was made by

the oven-dried sample of Soil No.II only it was more pronounced. The untreated sample of the latter soil increased about 0.3 ton, the air-dried decreased about 0.6 ton, and there was a slight rise in the ignited sample under the conditions of this sub-treatment.

The results obtained here with the oven-dried samples in particular which show a greater deviation from the field condition in proportion to the amount of organic matter present in the two soils seem to confirm the findings of Ritter (33), Rahn (32) and Klein (22) and others in regard to changes in the amounts of soluble matter and the bacterial activity produced by drying soils.

With one exception, all of the samples of this 25% moisture sub-treatment had less acidity at the end of twelve weeks than they had at the beginning of the experiment; and all of the samples of Soil No.I and the untreated sample of Soil No.II had less than they had at the end of the third week. The ignited sample of Soil No.II had increased slightly. The air-dried and oven-dried samples had recovered some of their acidity by the end of the sixth week but were losing it again by the end of the twelfth week although it had not reached quite the low level that it had at the end of the third week in either sample.

A sub-treatment of 50% moisture resulted in a depression of the acidity in every sample save the ignited sample of Soil No. II at the end of the three-week period. The greatest depressions were again with the oven-dried samples,

and the least were with the untreated samples not taking the ignited sample just mentioned into account. Each sample of the sub-treatment was less acid at the end of twelve weeks than it was at the beginning. A gradual reduction continued in the acidity after three weeks in the oven-dried samples of both soils, save one slight exception, and the untreated and ignited samples of Soil No.II, while an increase occurred in every other instance, except one.

The 100% moisture sub-treatment also showed depressions similar to those of the 25% and 50% sub-treatments at the end of three weeks. Likewise, with the exception of the untreated sample of Soil No.II, each sample showed a lower lime-requirement at the end of the twelve-week period. No particular reason can be ascribed to account for this exception. The ignited samples of both soils and the untreated sample of Soil No.I were the only samples which did not recover some of their acidity after the third week, but there was a slight recovery at the end of six weeks.

At the end of the twelfth week the remaining portions of all the duplicate samples used in the sub-treatments of the experiment were oven-dried for twenty-four hours at a temperature of 100^{o} - 105^{o} C. and then another determination of their lime-requirements was made.

Tables VII and VIII show the results of this oven-drying. First, it is observed that the treatment increased the lime-requirement of all of the samples except three of the ignited samples. Two of these were unaltered and the third showed a very slight decrease.

Not considering the ignited samples of either soil, the oven-dried samples which received the 100% moisture sub-treatment showed the least increase in acidity following the second oven-drying. Neither of these 100% moisture samples recovered the acidity which it had at the first oven-drying, but where 25% and 50% moisture was added there was practically a complete recovery in the case of the oven-dried samples of Soil No.11. In this soil the moisture-free sample, which had been previously oven-dried, showed a decided increase and the result is comparable with that of the sample which had remained untreated and received no sub-treatment except for the final oven-drying.

The results obtained from similarly treated samples of Soil No.1 were quite different. None of the oven-dried samples of this soil, regardless of the amount of moisture which had been added, recovered the acidity which the original oven-dried sample had possessed at the beginning of the experiment, but the moisture-free sample showed a little more acidity than the sample which had remained untreated in any way previous to this wholesale oven-drying.

In no instance did the air-dried samples of Soil No.1 reach the lime-requirements of the original oven-dried portion of this soil; but, where the 25% and 50% moisture sub-treatments were made, the results reached the highest level of any after all of the samples had been oven-dried the last time. The results of the air-dried samples of Soil No.11

Table VII

Effect of oven-drying upon the lime-requirements of Soil No.I after being kept at various moisture contents for twelve weeks.

Untreated

Moisture	34.9%	#59.9%	*84.9%	*134.9%
After drying	2.34	2.59	2.55	2.36
Before drying	1.98	1.80	1.93	1.90
Differences	0.36	0.79	0.62	0.46

Air-Dried

Moisture	2.7%	27.7%	*52.7%	*102.7%
After drying	2.28	2.59	2.57	2.05
Before drying	1.35	1.85	1.83	1.88
Differences	0.93	0.74	0.74	0.17

Oven-Dried

Moisture	0%	25%	*50%	*100%
After drying	2.42	2.34	2.41	1.80
Before drying	2.10	1.37	1.54	1.75
Differences	0.32	0.97	0.87	0.05

Ignited

Moisture	0%	#25%	*50%	*100%
After drying	0.56	0.55	0.41	0.40
Before drying	0.58	0.40	0.36	0.34
Differences	− 0.02	0.15	0.05	0.06

Table VIII

Effect of oven-drying upon the lime-requirements of Soil No.II after being kept at various moisture contents for twelve weeks.

Untreated

Moisture	61.4%	86.4%	#111.4%	*161.4%
After drying	4.28	4.43	4.01	4.13
Before drying	2.87	2.77	2.78	3.47
Differences	1.41	1.66	1.23	0.66

Air-Dried

Moisture	2.7%	27.7%	52.7%	*102.7%
After drying	4.09	4.12	4.06	3.69
Before drying	2.90	2.75	3.30	3.18
Differences	1.19	1.37	0.76	0.51

Oven-Dried

Moisture	0%	25%	50%	*100%
After drying	4.27	3.82	3.80	3.46
Before drying	3.37	2.35	2.19	3.26
Differences	0.90	1.47	1.61	0.20

Ignited

Moisture	0%	25%	5 0%	*100%
After drying	0.34	0.27	0.23	0.25
Before drying	0.20	0.27	0.23	0.23
Differences	0.14	0.00	0.00	0.02

were very similar. Here again, the depressing action of the 100% moisture treatment was evident. The samples recovered their original acidity but that of Soil No.I did not show as much of it as the original oven-dried moisture-free sample did, while that of Soil No.II showed much more. Oven-drying the air-dried sample of Soil No. II which had 100% moisture applied to it for twelve weeks increased in lime-requirement much more than did the corresponding sample of Soil No.I.

Oven-drying all of the samples of the untreated soil, regardless of the moisture sub-treatment which they received during the twelve week period, greatly increased their lime-requirements. The soil having the greatest organic content, which was Soil No.II, showed the largest increase. These results were the highest which had ever been obtained ~~before~~ with this soil under any treatment or sub-treatment, although the same did not hold true with Soil No.I. Where the 25% moisture sub-treatment had been applied to either untreated soil the largest final result was obtained.

Summary of Part I

The results obtained under the controlled conditions of the experiment and the methods used seem to indicate that:

1. The moisture content of acid soils influences their lime-requirements.

2. The influence varies with different soils.

3. Reduction of the moisture by air-drying slightly increases the acidity of a soil rather rich in organic matter, but the same process has a tendency to reduce the acidity of a soil which has a more mineral constituency although to a lesser degree.

4. Reducing the moisture by oven-drying materially increases the lime-requirement. Oven-drying the same samples again after twelve weeks had elapsed showed another increase in addition proportionately as large as that obtained after the first drying.

5. A slight decrease in acidity usually occurs as time goes on in the case of untreated, air-dried, and oven-dried samples of soils of variable moisture content which are occasionally stirred. The most pronounced change is in the oven-dried samples, and the least is in the untreated samples.

6. Air-dried and oven-dried samples of soils kept at a moisture condition which causes an inch or so of water to cover their surfaces apparently lose some of the properties which cause acidity in soils.

7. Soon after moisture is added to soils, regardless of the amount of moisture added or the previous treatment of the soil, a depression in the lime-requirement of those soils usually occurs. Then, the lime-requirement may become more or less, or may fluctuate rather inconsistently as time goes on.

PART II

THE RELATIONSHIPS OF CHANGES PRODUCED BY ALTERED MOISTURE CONDITIONS, OF THE LIME REQUIREMENT, HYDROGEN ION CONCENTRATION, AND WATER-EXTRACTABLE IRON AND ALUMINUM CONTENT OF ACID SOILS.

After the results recorded in Part I had been completed, a repetition of the study was started and continued for a short time to see if the performance of the soils would be the same. Another soil, Soil No.III, was added this time to compare its deportment with the ones already used.

Determination of the hydrogen ion concentrations, or pH values, and of the amounts of iron, aluminum, and manganese present in a soluble state in the extracts of the soils obtained by the use of water alone were attempted in an endeavor to explain, in part at least, the influence which the changes in moisture content of acid soils exert upon their soil solutions. These three soil elements were selected because they are believed to be partially responsible for the acidity of soils.

Preparation and Treatment of Soils for Experiment.

Some more composite samples of Soil No.I and Soil No.II were collected from the same areas from which they were

obtained before, and Soil No.III was collected from the area described above and immediately packed in a moisture-proof container for shipment to the laboratory. The same procedure was followed in the rest of the preparation of the treatments and sub-treatments as it has been described in Part I with the exception of the air-drying. Since the weather at this time was more favorable than it was at the previous time of drying, only about ten days were necessary instead of a month to accomplish the same result.

The same method was also employed for the determination of the lime requirements of the various samples.

The colorimetric methods for the determinations of the elements in the water extracts were necessarily used since the amounts of soils available were limited. When the soil was diluted to the same volume as that used for the lime requirement determinations these methods were found to be not sensitive enough to give differences which were satisfactory. One of two alternatives was possible. The amount of dilution could be lessened, or else the extract resulting from the above dilution could be concentrated by evaporation. Since this would mean that heat would have had to be applied in the latter instance, the former was considered the better procedure of the two. A one to five dilution was then finally adopted.

Methods of Analysis of the Soil Extracts.

Determination of the pH Values of Water Extracts of Soils.

The method described by Clark and Lubs (6) was employed. It is a colorimetric method based upon the behavior of indicators at various hydrogen ion concentrations. The reader is respectfully referred to their publication for the details regarding the preparation of the reagents and the apparatus used, for a discussion of them here seems unwarranted.

Standard solutions* as prescribed were prepared to cover a range of pH values from 4 to 7 with 0.2 intervals using M/5 KH Phthalate, M/5 NaOH, and M/5 KH_2PO_4. The solutions of unit pH value, e. g., pH 4,5,6, and 7, were checked electrometrically by the hydrogen electrode apparatus and were found to be pH 4.05, 5.10, 6.03, and 7.02. respectively. Portions of 5cc. of each standard solution were transferred into 1 x 10 cm. clear glass test-tubes and the respective indicators were added. Methylred was used for the range between pH 4 and 5.8 and bromthymol blue for that between 6.0 and 7.0, inclusively.

The indicator was added to 5cc. portions of the soil extract in a test-tube of the same size as those contain-

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*The author is indebted to Dr. A. Itano of the Department of Microbiology for the preparation of the standard solutions and for checking them by his hydrogen electrode apparatus. (17)

ing the standard solutions. The resulting coloration was compared with those of the standard solutions in the presence of equal portions of the soil extract without indicator and also distilled water. Comparisons of the colors of the menisci as well as those produced by the depth of solution, various backgrounds, and degrees of light were made before the final results were recorded.

Determination of Iron in the Water Extract of Soils.

A modification of the method described by Schreiner and Failyer (39) of the Bureau of Soils of the United States Department of Agriculture was used. This method makes use of the well known red colorization produced by sulphocyanates. The red color reaction is due, according to Noyes (Qualitative Chemical Analysis, 1918, p. 76, note) to the formation by metathesis of ferric thiocyanate, $Fe(CNS)_3$, a slightly ionized substance. Much HNO_3 present in solution produces a similar red colored compound which is unstable. The test is extremely delicate.

Analytical process.

An evaporating dish containing 10cc. of the acid soil extract to which 1 cc. of dilute nitric acid has been added is placed in an oven at a temperature $80^{\circ}C$ to $90^{\circ}C$, or on a water bath. The liquid is evaporated to small bulk (1 - 1.5 cc.), allowed to cool, and is than washed into a thin calibrated test-tube or 10 cc. graduate after the sides

of the dish have been thoroughly rubbed. The evaporating dish is rinsed with water until the total volume of the liquid is about 3 cc. 1 cc. of potassium sulphocyanate solution is then added before making the volume up to 10 cc. Comparison is made with a standard colorimetric solution prepared at the same time. (A comparator manufactured by the Klett Manufacturing Company of New York was used.)

Remarks.

Much difficulty was experienced in an endeavor to use the method just as described by the Bureau of Soils. Finally, after much study of the reactions which took place with the soils under the various treatment was made, the above modification to fit the conditions of the experiment was adopted.

The addition of nitric acid to either the standard of unknown extract in the quantity prescribed by the standard method caused the formation of an unstable compound which varied instantaneously. The color produced disappeared after a short time and left the solution colorless.

Should the soil extract after it had been evaporated to effect an oxidation of the ferrous iron to a ferric condition appear basic, hydrochloric acid was added drop by drop to bring out the blood red reaction before the final dilution was made.

Where the oven-dried and air-dried treatment extracts imparted a yellowish hue to the colorization, a more satisfactory comparison was found possible if a few drops of

bromthymol blue were added to the standard solution.

Determination of Aluminum in the Water Extracts of Soils.

The method used to determine the amount of aluminum present in the soil extracts is that suggested by Atack (1) for the determination of aluminum in steel, with a few modifications which were necessary to adapt it to the conditions of the experiment.

This method is a colorimetric one also. The indicator used is a filtered solution of commercial Alizarine S., the sodium salt of alizarine monosulphonic acid, which is yellow in acid and pruple in alkali. A very large excess is employed. "Precipitation of the aluminum which takes place most readily in the presence of other metals is prevented by glycerine." "The red calcium, strontium, barium, zince, and manganese salts, and the salts of other metals later than Group II are readily soluble in dilute acetic acid and do not interfere with the colorization. Phosphates or chromium do not interfere and comparatively large amounts of iron may be present (0.003 milligrams AL in presence of 1.0 milligrams of ferric iron, 10.0 milligrams of chromium salt). In the presence of larger quantities of iron, citric acid is added to keep this in solution." The delicacy of the test is such that 1 part of aluminum may be detected in 10 million parts of water. Colorations are compared soon after their formation because the acetic acid present gradually attacks

the finely divided aluminum precipitate which is red in suspension.

Reagents required.

1. Sulphuric acid - concentrated.

2. Clycerine - C.P. commercial.

3. Standard Alizarine S. Solution - 1% filtered solution of commercial product.

4. Ammonium Hydroxide - 15 normal.

5. Citric Acid - Dissolve 10 gm. of crystalline citric acid in water and make up to 100 cc. (This reagent is necessary only when the amount of iron and chromium salts is large. Double citrates are formed with these elements.)

6. Acetic Acid - 6 normal.

7. Standard Aluminum Solution* - Dissolve 1.6733 gm. of pure recrystalized ammonium aluminum sulphate, $AL_2(SO_4)(NH_4)_2SO_4.24H_2O$, in water and dilute to one liter. Dilute 100 cc. of this dilute solution to 1 liter. This dilute solution constitutes the standard, and each cubic centimeter contains 0.01 milligram of AL.

8. Standard Colorimetric Solution - This may be prepared by diluting 5 cc. of the standard aluminum solution, above, to 50 cc. This colorimetric standard contains 1 part AL per million parts of water.

Analytical process.

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*The use of ammonium aluminum sulphate was suggested by Professor F. W. Morse of the Experiment Station.

Acidify 5cc. of the soil extract with sulphuric acid. Add 10 cc. of glycerine and 5 cc. of 1% solution of Alizarine S. Render slightly ammoniacal at once. Add citric acid if necessary. Allow to stand 5 minutes. Acidify with acetic acid until there is no further change in the coloration, or until the meniscus shows a permanent yellow hue. Make the solution up to 50 cc. with water and compare with the standard immediately.

This method proved to be very efficient when the manipulations were properly performed.

In only one case was the addition of citric acid necessary. This was where an oven-dried sample had been covered with 100% of added moisture for six weeks.

Determination of Manganese in the Water Extract of Soils.

The original plans of the experiment made allowance for the determination of manganese in the water extracts in addition to those of iron and aluminum. Although there were indications of its presence, no satisfactory method could be found or worked out to give differences that were large enough to be read in the time allotted before the experiment began so that its determination was reluctantly abandoned.

Results of the Repetition of the Experiment Determining the Lime Requirements.

The second set of experiments which were run as a check

upon those recorded in Part I of this paper covered a period of six weeks. The determinations were made at the beginning, at the end of three weeks and the end of six weeks as before.

Table IX

Lime-requirements of Soil No.I at various moisture contents during a period of six weeks.

(Expressed in tons of CaO per acre 2,000,000 pounds)

Untreated

Moisture	34.0%	#59.0%	*84.0%	*134.0%
At beginning	2.45	2.45	2.45	2.45
End of 3rd week	2.32	2.34	2.33	2.45
" " 6th "	2.42	2.14	2.29	2.24

Air-Dried

Moisture	2.4%	27.4%	*52.4%	*102.4%
At beginning	1.98	1.98	1.98	1.98
End of 3rd week	1.96	2.07	1.94	1.80
" " 6th "	1.96	2.02	1.91	1.93

Oven-Dried

Moisture	0%	25%	*50%	*100%
At beginning	2.32	2.32	2.32	2.32
End of 3rd week	2.16	1.58	1.70	1.81
" " 6th "	2.14	1.42	1.88	1.80

Ignited

Moisture	0%	25%	*50%	*100%
At beginning	0.43	0.43	0.43	0.43
End of 3rd week	0.47	0.43	0.38	0.40
" " 6th "	0.40	0.34	0.36	0.36

Table X

Lime-requirements of Soil No.II at various moisture contents during a period of six weeks.

(Expressed in tons of CaO per acre 2,000,000 pounds)

Untreated

Moisture	51.6%	76.6%	#101.6%	*151.6%
At beginning	2.18	2.18	2.18	2.18
End of 3rd week	2.16	2.20	2.27	2.25
" " 6th "	2.22	2.09	2.25	2.14

Air-Dried

Moisture	4.5%	29.5%	54.5%	*104.5%
At beginning	2.96	2.96	2.96	2.96
End of 3rd week	2.79	2.71	2.27	3.24
" " 6th "	2.76	2.81	3.15	3.30

Oven-Dried

Moisture	0%	25%	50%	*100%
At beginning	3.28	3.28	3.28	3.28
End of 3rd week	3.17	2.56	2.61	3.36
" " 6th "	2.85	2.45	2.49	3.24

Ignited

Moisture	0%	25%	50%	*100%
At beginning	0.25	0.25	0.25	0.25
End of 3rd week	0.29	0.23	0.23	0.23
" " 6th "	0.22	0.22	0.22	0.22

Table XI

Lime-requirements of Soil No. III at various moisture contents during a period of six weeks.

(Expressed in tons of CaO per acre 2,000,000 pounds)

Untreated

Moisture	23.0%	48.0%	#73.0%	*123.0%
At beginning	1.62	1.62	1.62	1.62
End of 3rd week	1.65	1.77	1.48	1.31
" " 6th "	1.65	1.63	1.32	1.17

Air-Dried

Moisture	1.9%	26.9%	51.9%	*101.9%
At beginning	1.58	1.58	1.58	1.58
End of 3rd week	1.62	1.37	1.13	1.32
" " 6th "	1.50	1.46	1.17	1.44

Oven-Dried

Moisture	0%	25%	50%	*100%
At beginning	2.16	2.16	2.16	2.16
End of 3rd week	2.14	1.23	1.12	1.50
" " 6th "	2.00	1.12	1.08	1.58

Ignited

Moisture	0%	25%	#50%	*100%
At beginning	0.38	0.38	0.38	0.38
End of 3rd week	0.36	0.31	0.29	0.31
" " 6th "	0.29	0.25	0.25	0.29

Portions of the same air-dried samples of soil No.I and Soil No.II that were prepared for Part I were also used in this set. It was thought that a continuation of the deportment of these two samples where no moisture had been added could thus be studied. The oven-dried samples used were obtained also by oven-drying samples of this air-dry material.

The results are recorded in Tables IX and X. An examination of these tables shows that Soil No.I and Soil No. II, outside of a few particular instances, acted very much ~~like~~ they did the first time. The same general conclusions, can be drawn also.

The air-dried sample showed here that it was continuing to lose its acidity. This was true with both soils but Soil No.II showed the greatest decrease. Where 100% moisture was added to the air-dried and the oven-dried soil in Table X, an increase was produced which continued upwards in the air-dried sample but not in the oven-dried sample. A very large increase also occurred between the third and sixth week in the air-dried sample of Soil No.II where 50% moisture was added.

When the results of Table XI are compared with those of the other two tables it will be observed that the results obtained for Soil No.III are generally concordant with those of both Soil No. I and Soil No.II. The same relative decrease due to air-drying that was found with Soil No.I is discovered. Oven-drying likewise produced a large in-

crease. The general tendency for all samples to reach a lower level as time goes on is evidenced.

By the end of the third week, a blue-green mold had accumulated upon the surfaces of the 25% and 50% moisture sub-treated samples of Soil No.II. The same was present upon the surfaces of the 25% sub-treatments of both Soil No.I and Soil No.III.

A strong odor of putrefaction and a growth of white and blue-green molds were noticeable wherever the moisture percentage of the untreated, air-dried, or oven-dried samples of all three soils was sufficient to cause standing water to be present above the surface of the soil in the sample bottle.

Effect of Moisture Upon the pH Values of Water Extracts.

The results which are recorded in Tables XII, XIII, & XIV indicate that the changes in the moisture contents of all three acid soils had an effect upon the pH values, or the hydrogen-ion concentration, of their water extracts. Since a difference was produced in the water extracts, it is very likely that a change was wrought in the solution of these soils.

The hydrogen ion concentrations of the water extracts as measured by the pH values were roughly comparable with those results obtained by the lime-requirement measurements of the untreated samples of Soil No.I and Soil No.II, but there were no particular agreements of Soil No.III under

the same treatment and sub-treatments. Some correlation was found among the air-dried group of sub-treatments. Also, there was a similarity between the oven-dried

Table XII

pH values of water-extracts from Soil No.I at various moisture contents during a period of six weeks.

Untreated

Moisture	34.0%	#59.0%	*84.0%	*134.0%
At beginning	5.1	5.1	5.1	5.1
End of 3rd week	5.1	4.7	4.8	4.6
" " 6th "	4.8	4.8	5.3	5.0

Air-Dried

Moisture	2.4%	27.4%	*52.4%	*102.4%
At beginning	5.5	5.5	5.5	5.5
End of 3rd week	5.0	5.6	5.8	5.2
" " 6th "	6.1	5.2	6.4	5.2

Oven-Dried

Moisture	0%	25%	*50%	*100%
At beginning	4.9	4.9	4.9	4.9
End of 3rd week	5.0	6.0	6.0	5.8
" " 6th "	5.1	6.0	5.4	5.2

Ignited

Moisture	0%	25%	*50%	*100%
At beginning	5.8	5.8	5.8	5.8
End of 3rd week	5.0	6.5	6.5	6.6
" " 6th "	6.8	6.8	6.7	6.9

Table XIII

pH values of water-extracts from Soil No. II at various moisture contents during a period of six weeks.

Untreated

Moisture	51.6%	76.6%	#101.6%	*151.6%
At beginning	5.5	5.5	5.5	5.5
End of 3rd week	5.4	6.2	6.2	6.2
" " 6th "	5.7	6.3	6.1	6.2

Air-Dried

Moisture	4.5	29.5%	54.5%	*104.5%
At beginning	5.6	5.6	5.6	5.6
End of 3rd week	5.6	6.0	6.2	6.2
" " 6th "	5.6	6.3	6.2	6.2

Oven-Dried

Moisture	0%	25%	50%	*100%
At beginning	5.4	5.4	5.4	5.4
End of 3rd week	5.2	6.2	6.2	5.4
" " 6th "	5.4	6.2	5.8	5.5

Ignited

Moisture	0%	25%	50%	*100%
At beginning	6.8	6.8	6.8	6.8
End of 3rd week	6.6	6.6	6.8	6.8
" " 6th "	6.6	6.8	6.8	7.0

Table XIV

pH values of water-extracts from Soil No. III at various moisture contents during a period of six weeks.

Untreated

Moisture	23.0%	48.0%	#73.0%	*123.0%
At beginning	6.4	6.4	6.4	6.4
End of 3rd week	6.2	5.8	6.4	6.1
" " 6th "	6.2	6.7	6.6	6.5

Air-Dried

Moisture	1.9%	26.9%	51.9%	*101.9%
At beginning	6.6	6.6	6.6	6.6
End of 3rd week	5.9	5.8	6.4	6.2
" " 6th "	6.4	6.4	6.4	6.8

Oven-Dried

Moisture	0%	25%	50%	*100%
At beginning	6.6	6.6	6.6	6.6
End of 3rd week	5.3	5.8	6.2	5.8
" " 6th "	6.6	6.2	6.5	6.4

Ignited

Moisture	0%	25%	#50%	*100%
At beginning	6.6	6.6	6.6	6.6
End of 3rd week	6.4	6.2	6.4	6.4
" " 6th "	6.9	6.0	6.7	6.9

groups and also between the ignited ones, except with those of the latter in Soil No. III.

Effect of Moisture Upom the Iron Content of Water Extracts.

Tables XV, XVI and XVII show that there was a general increase in the amount of iron extracted with the length of time, regardless of the moisture subtreatment that the samples of the untreated soils received. The largest increases occurred with those sub-treatments where moisture was added. By the end of six weeks the greatest moisture application produced the greatest increase in the amount of iron. The other applications were arranged accordingly.

Considering the group of sub-treatments which had been previously air-dried, the iron again increased somewhat, except for the sample of Soil Nos. I and III which had not been remoistened. The 100% moisture sub-treatments showed the greatest increase over any other at the end of the third week in all three soils, but the greatest increase of all was with the sample of that sub-treatment of Soil No. I There was a marked decrease in the corresponding sample of Soil No. III by the end of the sixth week.

The oven-dried group made similar increases in the amounts of extractable iron and the increases continued in every sample except where 100% moisture had been added to Soil No. III Enormous amounts of iron, compared to the others, were extracted from the 50% and 100% sub-treatments of Soil No. I and the 100% sub-treatment of Soil No. II

A marked increase was also noticeable in the same sample of Soil No. III. These increases continued as time went on.

Table XV

Water-extractable iron of Soil No. I at various moisture contents during a period of six weeks.

(Expressed in pounds per acre 2,000,000 pounds)

Untreated

Moisture	34.0%	#59.0%	*84.0%	*134.0%
At beginning	trace	trace	trace	trace
End of 3rd week	2.33	2.38	2.27	3.50
" " 6th "	2.50	3.23	6.74	5.32

Air-Dried

Moisture	2.4%	27.4%	*52.4%	*102.4%
At beginning	trace	trace	trace	trace
End of 3rd week	2.76	2.38	3.33	64.58
" " 6th "	2.63	1.70	7.76	205.20

Oven-Dried

Moisture	0%	25%	*50%	*100%
At beginning	3.78	3.78	3.78	3.78
End of 3rd week	trace	trace	1.57	26.83
" " 6th "	3.72	6.92	210.40	133.95

Ignited

Moisture	0%	2 5%	*50%	*100%
At beginning	trace	trace	trace	trace
End of 3rd week	2.59	2.33	3.24	35.50
" " 6th "	2.31	1.83	3.35	5.54

Table XVI

Water-extractable iron of Soil No.II at various moisture contents during a period of six weeks. (Expressed in pounds per acre 2,000,000 pounds.

Untreated

Moisture	51.6%	76.6%	#101.6%	*151.6%
At beginning	trace	trace	trace	trace
End of 3rd week	4.05	4.23	trace	5.25
" " 6th "	1.54	6.39	14.43	8.89

Air-Dried

Moisture	4.5%	29.5%	54.5%	*104.5%
At beginning	5.82	5.82	5.82	5.82
End of 3rd week	14.76	11.44	11.90	20.11
" " 6th "	8.66	7.26	7.88	58.16

Oven-Dried

Moisture	0%	25%	50%	*100%
At beginning	5.85	5.85	5.85	5.85
End of 3rd week	trace	9.73	10.86	34.94
" " 6th "	trace	11.64	19.76	163.14

Ignited

Moisture	0%	25%	50%	*100%
At beginning	trace	trace	trace	trace
End of 3rd week	2.48	trace	trace	1.80
" " 6th "	1.67	1.38	10.54	4.70

Table XVII

Water-extractable iron of soil No.III at various moisture contents during a perion of six weeks. (Expressed in pounds per acre 2,000,000 pounds)

Untreated

Moisture	23.0%	48.0%	#73.0%	*123.0%
At beginning	trace	trace	trace	trace
End of 3rd week	3.50	3.33	5.69	17.39
" " 6th "	2.51	12.45	23.08	14.43

Air-Dried

Moisture	1.9%	26.9%	51.9%	*101.9%
At beginning	7.06	7.06	7.06	7.06
End of 3rd week	11.31	8.30	10.96	22.23
" " 6th "	6.19	8.21	22.92	7.88

Oven-Dried

Moisture	0%	25%	50%	*100%
At beginning	9.43	9.43	9.43	9.43
End of 3rd week	6.76	12.14	17.29	44.65
" " 6th "	5.72	18.02	45.31	19.76

Ignited

Moisture	0%	25%	50%	*100%
At beginning	trace	trace	trace	trace
End of 3rd week	8.63	6.33	8.07	12.53
" " 6th "	1.33	10.35	5.04	10.54

The changes produced in the amount of iron in the ignited group were negligible, except for one instance which occured at the end of the third week with Soil No. I where a 100% moisture treatment was made.

There was a general correlation between the changes in the amounts of iron produced by changes of the moisture content of the soil and the changes in the hydrogen ion concentration as measured by the indicator method and expressed in pH values of the water extracts of the three acid soils used in this study. And there was a correlation between the changes in the amounts of iron in the water extracts of the soils and the changes in the lime-requirements as measured by the calcium acetate method possible under the conditions of the experiment.

Effect of Moisture Upon the Aluminum Content of Water Extracts.

The data recording the effect of variations in the moisture content of acids soils upon the amount of aluminum in their water extracts are found in Tables XVIII, IXX & XX.

An increase in the ampunts of aluminum present in the extracts of the untreated groups of all three soils at the end of six weeks was observed. The increase, however, was much greater at the end of three weeks in the majority of instances. Where moisture additions were made there was an increase in the amount of aluminum, but an increase in moisture did not always produce a corresponding increase in the aluminum extracted.

Table XVIII

Water-extractable aluminum of Soil No.I at various moisture contents during a period of six weeks.

(Expressed in pounds per acre 2,000,000 pounds)

Untreated

Moisture	34.0%	#59.0%	*84.0%	*134.0%
At beginning	5.87	5.87	5.87	5.87
End of 3rd week	5.78	17.85	18.62	26.39
" " 6th "	6.94	8.78	12.91	11.93

Air-Dried

Moisture	2.4%	27.4%	*52.4%	*102.4%
At beginning	5.19	5.19	5.19	5.19
End of 3rd week	6.14	14.78	16.27	17.55
" " 6th "	8.16	10.05	12.78	12.43

Oven-Dried

Moisture	0%	25%	*50%	*100%
At beginning	3.86	3.86	3.86	3.86
End of 3rd week	12.12	13.17	16.90	17.13
" " 6th "	5.86	11.17	12.31	12.06

Ignited

Moisture	0%	25%	*50%	*100%
At beginning	4.58	4.58	4.58	4.58
End of 3rd week	6.40	12.08	15.02	19.24
" " 6th "	7.74	9.49	10.65	13.68

Table XIX

Water-extractable aluminum of Soil No. II at various moisture contents during a period of six weeks.

(Expressed in pounds per acre 2,000,000 pounds)

Untreated

Moisture	51.6%	76.6%	#101.6%	*151.6%
At beginning	5.87	5.87	5.87	5.87
End of 3rd week	12.35	14.72	15.09	17.25
" " 6th "	7.52	11.63	17.59	13.54

Air-Dried

Moisture	4.5%	29.5%	54.5%	*104.5%
At beginning	9.08	9.08	9.08	9.08
End of 3rd week	10.53	11.46	12.42	17.27
" " 6th "	5.47	14.56	16.23	14.22

Oven-Dried

Moisture	0%	25%	50%	*100%
At beginning	15.32	15.32	15.32	15.32
End of 3rd week	5.06	16.27	11.99	20.73
" " 6th "	8.08	14.29	13.10	12.20

Ignited

Moisture	0%	25%	50%	*100%
At beginning	12.10	12.10	12.10	12.10
End of 3rd week	10.06	21.25	24.95	23.58
" " 6th "	5.89	13.01	11.39	12.45

Table XX

Water-extractable aluminum of Soil No. III at various moisture contents during a period of six weeks.

(Expressed in pounds per acre 2,000,000 pounds)

Untreated

Moisture	23.0%	48.0%	#73.0%	*123.0%
At beginning	4.84	4.84	4.84	4.84
End of 3rd week	4.51	5.31	12.74	8.10
" " 6th "	6.58	7.25	10.02	7.71

Air-Dried

Moisture	1.9%	26.9%	51.9%	*101.9%
At beginning	3.76	3.76	3.76	3.76
End of 3rd week	4.23	6.44	14.72	13.01
" " 6th "	5.33	6.48	11.53	6.46

Oven-Dried

Moisture	0%	25%	50%	*100%
At beginning	7.54	7.54	7.54	7.54
End of 3rd week	9.48	8.43	10.26	13.87
" " 6th "	4.68	4.87	8.63	7.27

Ignited

Moisture	0%	25%	50%	*100%
At beginning	5.82	5.82	5.82	5.82
End of 3rd week	2.65	8.05	12.13	10.73
" " 6th "	3.62	4.70	7.33	8.41

All of the differences were generally alike in the air-dried group of sub-treatments. Moisture additions caused an increase in every instance in every soil. In the majority of cases, the amount of aluminum was less at the end of six weeks than at the end of three weeks.

The amounts of aluminum present in the water extracts of the group of sub-treatments which were previously oven-dried showed the same general agreement. There was also a marked similarity for the samples which had been ignited. In fact, there was a more or less general agreement among the results obtained from all of the treatments and sub-treatments of the three soils.

Here again as with the iron, the amounts of aluminum in the water extracts of the soils under various moisture treatments seemed to have some correlation with the intensity of the acidity of the soils, measured either by the hydrogen-ion concentration of their water extracts, or the lime-requirement method.

Furthermore, the sums of the amounts of iron and aluminum, recorded in Tables XXI, XXII, & XXIII give some indication of correlation with the differences in the lime-requirements of the three acid soils, produced by changes in their moisture contents.

Summary of Part II.

The results obtained from the methods used in this part of the work seem to indicate that:

1. The conclusions summarized at the end of Part I were also applicable to the results obtained for the determ-

Table XXI

Water-extractable iron plus water-extractable aluminum of Soil No.I at various moisture contents during a period of six weeks.
(Expressed in pounds per acre 2,000,000 pounds)

Untreated

Moisture	34.0%	#59.0%	*84.0%	*134.0%
At beginning	5.87	5.87	5.87	5.87
End of 3rd week	8.11	20.23	20.89	29.89
" " 6th "	9.44	12.01	19.65	17.25

Air-Dried

Moisture	2.4%	27.4%	*52.4%	*102.4%
At beginning	5.19	5.19	5.19	5.19
End of 3rd week	8.90	17.16	19.60	82.13
" " 6th "	10.79	11.75	20.54	217.63

Oven-Dried

Moisture	0%	25%	*50%	*100%
At beginning	7.64	7.64	7.64	7.64
End of 3rd week	12.12	13.17	18.47	43.96
" " 6th "	9.58	18.09	222.71	146.01

Ignited

Moisture	0%	25%	*50%	*100%
At beginning	4.58	4.58	4.58	4.58
End of 3rd week	8.99	14.41	18.26	54.74
" " 6th "	10.05	11.32	14.00	19.22

Table XXII

Water-extractable iron plus water-extractable aluminum of Soil No. II at various moisture contents during a period of six weeks.
(Expressed in pounds per acre 2,000,000 pounds)

Untreated

Moisture	51.6%	76.6%	#101.6%	*151.6%
At beginning	5.87	5.87	5.87	5.87
End of 3rd week	16.30	18.95	15.09	22.50
" " 6th "	9.06	28.02	32.02	22.43

Air-Dried

Moisture	4.5%	29.5%	54.5%	*104.5%
At beginning	14.90	14.90	14.90	14.90
End of 3rd week	25.29	22.90	25.32	37.38
" " 6th "	14.13	21.82	24.11	72.38

Oven-Dried

Moisture	0%	25%	50%	*100%
At beginning	21.17	21.17	21.17	21.17
End of 3rd week	5.06	26.00	22.85	55.67
" " 6th "	8.08	25.93	32.86	175.34

Ignited

Moisture	0%	25%	50%	*100%
At beginning	12.10	12.10	12.10	12.10
End of 3rd week	12.54	21.25	24.95	25.38
" " 6th "	7.56	14.39	21.93	17.15

Table XXIII

Water-extractable iron plus water-extractable aluminum of Soil No. III at various moisture contents during a period of six weeks.
(Expressed in pounds per acre 2,000,000 pounds)

Untreated

Moisture	23.0%	48.0%	#73.0%	*123.0%
At beginning	4.84	4.84	4.84	4.84
End of 3rd week	8.01	8.64	18.43	25.49
" " 6th "	9.09	19.70	33.10	22.14

Air-Dried

Moisture	1.9%	26.9%	51.9%	*101.9%
At beginning	10.82	10.82	10.82	10.82
End of 3rd week	16.54	14.74	25.68	35.24
" " 6th "	11.52	14.67	34.45	14.34

Oven-Dried

Moisture	0%	25%	50%	*100%
At beginning	16.97	16.97	16.97	16.97
End of 3rd week	16.24	20.57	27.55	58.52
" " 6th "	10.40	22.89	53.94	17.03

Ignited

Moisture	0%	25%	50%	*100%
At beginning	5.82	5.82	5.82	5.82
End of 3rd week	11.28	14.38	20.20	23.26
" " 6th "	4.95	15.05	12.37	18.95

ination of the lime-requirements in Part II for Soil No.III, in addition to those of Soil No.I and Soil No.II.

2. The pH values of the water extracts from the soil samples also gave indication of differences in the acidity produced by the changes in the moisture contents of the soils.

3. Changes in the moisture contents of the soils produced changes in the amounts of iron in their water extracts.

4. Changes in the moisture contents of the soils produced changes in the amounts of aluminum in their water extracts.

5. The measurements of the intensity of acidity in the water extracts of the soils, variously treated in regards to their moisture content, expressed in terms of pH, and made by the indicator method of Clark and Lubs, were found similar to those measurements which were made by the modification of Jones Method used for the determination of the lime-requirements of the soils, except for the air-dried samples of Soil No.III, the untreated samples of Soil No.II and Soil No.III, and the ignited samples of Soil No.III.

6. The amounts of iron extracted from the soils showed some correlation with the expressions of the intensity of acidity of the soils, either as pH values of the water extracts or as lime-requirements. The solubility of iron increased as the acidity measured by both methods decreased.

7. The amounts of aluminum extracted from the soils showed some correlation with the expressions of the intensity of acidity of the soils, either as pH values of the water

extracts or as lime-requirements. An increase in the solubility of aluminum was noted in the majority of cases.

8. Likewise, the sums of the iron and the aluminum found in the water extract and the pH values were more or less in agreement with each other or with the lime-requirements of the soils. There was an increase with the moisture content and also with the length of time.

PART III

THE CORRELATION OF CHANGES PRODUCED BY AIR-DRYING, OF THE LIME REQUIREMENT, HYDROGEN ION CONCENTRATION, AND WATER-EXTRACTABLE IRON AND ALUMINUM CONTENT WITH THOSE OF THE CROP-PRODUCING POWER OF ACID SOILS.

An attempt was made to study the influence exerted upon acid soils when a reduction of their moisture contents was accomplished by air-drying the soils previous to planting. Results were sought chiefly with soils bearing a crop for a considerable length of time after treatment. At first, a correlation of the differences in the lime requirements of the soils with those in the crop-producing powers was to be made if possible when this part of the experiment was planned. Later, when the work of Part II was in progress it was decided to include the differences produced in the pH values and the iron and aluminum contents of the water extracts of the soils in the correlation along with those in the lime requirements.

Preparation for the Experiment

Untreated and air-dried samples of Soil No.I and Soil No.II obtained as those described in the preparation of soils in Part I above, were placed in one-gallon pots after

the air-dried soil had been remoistened. The lime-requirements of the soils at this time were found to be 2.11 tons and 2.04 tons for the untreated and air-dried samples of soil No.I, respectively,and 3.12 tons and 3.33 tons of CaO per acre 2,000,000 pounds for the samples of Soil No.II

Observations upon the Growth of Crops on Untreated and Previously Air-dried Soil Samples.

On January 1, 1920, the soils in the pots were planted in duplicate to rye, red clover, and barley so that there were duplicate pots of untreated and air-dried samples of soil of each kind planted for each crop. The pots were then placed in the greenhouse.

Since the moisture content of the untreated samples were above optimum no more moisture was added to them for several days, but the air-dried samples were watered twice a day in an endeavor to keep them up to optimum moisture content.

At the end of twelve weeks, the rye and barley were thinned to ten plants to a pot. It was observed at this time that some of the root-systems of the barley plants removed from the untreated samples of Soil No.I showed some injury from the apparent presence of some toxic substance. The percentage of germination in all of the pots of both soils was very good, but many of the clover seedlings on Soil No.I soon died out. Only the strongest of the plants were able to withstand the toxic property of the soil.

Chlorosis was prominent on all of the clover of this soil, but more so on the air-dried samples.

There were indications of rust upon the barley plants of Soil No.I by the 20th of January. A blue-green, and in places, a white mold covered the surfaces of all the samples of this same soil if they were not mulched every few days. A very good stand as well as good growth was produced upon samples of Soil No.II regardless of the previous treatment of the soil. The air-dried samples of both soils in every instance seemed to be producing a crop which was darker green than the corresponding untreated samples.

By February 20th, the clover on Soil No.II was making rapid progress, but that on Soil No.I showed very poor retarded growth in spite of the fact that there were fewer plants per pot. A plant of sheep sorrel (R. Autmen) had begun to grow in one of the untreated soil pots. An oat plant was discovered in one of the air-dried pots containing barley also. Since the growth in both of these pots was poor it was decided to let these two foreign plants remain. With the exception of the growth of rye, the growth of all the crops on Soil No.II exceeded that of Soil No.I. The barley was much more vigorous on the untreated samples of the latter soil than upon the air-dried samples.

The same general comparison existed between the growth of the crops in the untreated and the air-dried pots of both soils by the end of March. A few of the clover plants

in the untreated pots of Soil No.I had reached a height of four inches while the others were still about three-quarters of an inch high and looked sickly.

Great difficulty was experienced in trying to keep the air-dried samples at optimum moisture content. They seemed to dry out very rapidly. This fact was particularly true of Soil No.I

The barley started to head out on all of the soils at about the same time. The first marked indications of heading were observed upon April 9th. The rye did not start to head until the first of May. At the latter date the depth of color in favor of the soils which were previously air-dried was still in evidence, in fact, it continued throughout the growing of the crops. No radical changes appeared from this time on.

The photographs accompanying this paper were taken on the 20th of July when the barley and rye were about mature. Two weeks later the crops were harvested with all of the roots that could possibly be removed with them. All of the barley, which is a shallow feeder, ~~had its~~ roots penetrated the soil for a few inches in every pot. The larger roots of the clover were found near the edge of the soils, except where the soils had been previously air-dried. In the air-dried samples the roots penetrated the whole soil mass. In every instance the large roots of the rye found their way to the bottom of the pots between the soil and the side of the pot. No roots seemed to penetrate more than

an inch or two below the surface in any other part of the soil. The harvested crops were spread out in the greenhouse to dry and they were photographed later when the weights in the moisture free condition were taken.

Treatment of Soil Samples for Analysis

As rapidly as the crop in each pot was harvested, a composite sample of the soil was taken. Just as soon as all the harvesting was done a composite sample representing the moisture condition in each pot was taken directly to the soil laboratory and placed in an oven to be dried at 100°C to 105°C for twenty-four hours. At the end of twenty-four hours the soil was rapidly crushed and rolled with a wooden rolling pin, placed in a covered soil box while still warm, and the box was placed in a desiccator until the analysis could be made about a week later.

Results of Analysis.

The results of the analysis are found in Tables XXIV and XXV. The first column gives the crops grown, whereas the second gives the respective treatment of the soil in the pots supporting these crops before they were planted in the soil. The dry weight of the crops produced upon the soils and recorded in the fourth column represent the crop producing power of the soil. All of the data in the last four columns represent duplicate determinations made upon the samples of soil in the pots.

Table XXIV Results of pot experiment showing the effects of air-drying Soil No.I previous to planting.

Crop	Treatment of soil previous to planting.	Number of pot.	Air-dry weight of crop (grams).	Moisture condition of soil at harvest.	Lime-Requirement (tons CaO)	pH Value	Water-Extractable Iron (pounds)*	Water-Extractable Aluminum (pounds).*
Barley	Untreated	1AB1	12.00	moist	1.93	6.0	1.81	3.98
		1AB2	12.10	moist	1.89	6.0	1.58	4.60
	Air-Dried	1BB1	12.00	moist	1.80	6.3	1.61	2.90
		1BB2	°21.00	fairly dry	1.78	6.3	1.29	2.56
Clover	Untreated	1AC1	°17.00	wet	2.16	5.6	2.24	1.92
		1AC2	12.15	wet	2.12	5.6	2.42	1.82
	Air-Dried	1BC1	14.65	fairly dry	1.93	5.6	2.41	2.12
		1BC2	#11.70	fairly dry	1.80	5.6	2.01	1.40
Rye	Untreated	1AR1	22.00	moist	2.06	5.0	2.04	1.42
		1AR2	20.50	moist	1.98	5.0	2.33	1.24
	Air-Dried	1BR1	18.00	dry	2.09	4.8	2.35	2.34
		1BR2	24.45	dry	2.27	4.8	2.26	2.00

°oats, 13.00 grams (Barley, 1BB2)

°sorrel, 13.65 grams (Clover, 1AC1)
#grass, 1.25 " (Clover, 1BC2)

*per acre 2,000,000 pounds

Table XXV Results of pot experiment showing the effects of air-drying Soil No.II previous to planting.

Crop	Treatment of soil previous to planting.	Number of pot.	Air-dry weight of crop (grams).	Moisture condition of soil at harvest.	Lime-Requirement (tons CaO).	pH Value.	Water-Extractable Iron (pounds)*	Water-Extractable Aluminum (pounds) *
Barley	Untreated	2AB1	16.90	fairly dry	3.71	5.4	1.77	3.82
		2AB2	18.20	moist	3.37	6.0	1.75	4.94
	Air-Dried	2BB1	20.70	dry	3.22	5.8	1.82	2.90
		2BB2	17.20	dry	3.23	6.0	1.70	1.96
Clover	Untreated	2AC1	34.60	wet	3.26	6.4	1.05	2.28
		2AC2	25.00	very wet	2.99	6.4	1.69	1.52
	Air-Dried	2BC1	28.30	dry	2.97	6.2	1.84	2.66
		2BC2	31.30	dry	2.97	6.2	1.78	2.60
Rye	Untreated	2AR1	23.35	wet	3.80	4.4	2.43	2.78
		2AR2	23.60	wet	3.91	4.6	2.50	2.48
	Air-Dried	2BR1	19.00	dry	3.60	4.4	2.48	2.48
		2BR2	18.00	moist	3.65	4.4	3.33	2.42

*per acre 2,000,000 pounds

Conclusions

During the time which the soils were producing crops, it is apparent that changes occurred in the lime requirement of the soils. The moisture content of the soils fluctuated more or less during the growth of the crops, undoubtedly. Only three samples of Soil No.I showed an increase in lime requirement at the time of harvest over that at the time of planting, regardless of the previous treatment of the soil, and then the increases were small. The reverse was true of Soil No.II. Only five samples of the twelve showed a decrease and these decreases were small compared with the increases of the other seven samples. Six of the increases exceeded that which was caused by the air-drying at the beginning of the experiment.

There seemed to be some correlation between the moisture conditions at the time of harvest and the lime requirements of the samples of either soil. In all but one case, the rye on Soil No.II, the soils that had been previously air-dried had the lower lime requirement at the end of the experiment. Air-drying the soils previous to planting had a tendency to retard the accumulation of the compounds responsible for the soil acidity in nearly every instance .

Barley and clover, when they were grown upon either soil, seemed to exert a depressing influence upon the abil-

ity of the soils to increase their lime requirements. If increases were produced, they did not compare with the increases in lime requirement of the samples supporting rye. Marked increases were more apparent with the later crop, especially in Soil No.II which contained considerable more organic matter than Soil No.I. The greater the weight of the crop of rye produced the greater the intensity of the acidity of the soil became. When the soils had been previously air-dried before planting, samples of Soil No.I supporting rye were the only soils which did not show less lime requirement than the corresponding untreated samples.

The water-extractable iron and aluminum did not seem to bear any relationship to the pH values of the water extracts from which they were derived, nor could the pH values of these water extracts be correlated with the corresponding lime requirements of the soils in any satisfactory manner. In some instances there is a rough comparison of increase in the amounts of aluminum and iron with those in pH value, lime requirement and moisture. Such a comparison is more obvious where barley and rye were grown as crops than where clover was grown.

The previous air-drying has had an influence upon the results as well as the oven-drying of the samples at the end of the experiment and the moisture conditions at that time.

Summary of Part III

The results obtained under the conditions of this part of the work seem to indicate that:

1. While crops are growing upon soils, the lime requirements of these soils vary.

2. The degree of change is dependent upon moisture conditions.

3. Whether the change is positive or negative is usually dependent upon the organic content of the soil. The soils rich in organic matter have a tendency to increase in acidity, measured either as lime requirement or hydrogen ion concentration, other soils decrease.

4. The treatment of the soil previous to planting a crop upon it, where the moisture content is altered, produces somewhat different results than when the soil is left untreated.

5. Air-drying a soil previous to planting helped to retard the accumulation of those substances which cause soil acidity during the growth of the crop.

6. Of the three crops grown, the weights of rye harvested from the various soil samples were the only ones which bore any relationship to the amounts of lime required by the samples at the end of the period of crop growth.

7. Barley and clover did not permit the intensity of the soil acidity to increase as much as the rye did.

8. There were some indications that the changes, produced by air-drying, of the lime requirement, hydrogen ion concentration, and water-extractable iron and aluminum of

acid soils bore relationships to each other and to the crop-producing power of these soils although the moisture contents of the samples were not alike and the oven-drying at the end of the experiment spoiled the influence of the previous treatment.

GENERAL SUMMARY

A change in the moisture content of acid soils usually produced a change in their lime requirement, regardless of the particular alteration, type of soil, or previous treatment.

The variations in the hydrogen ion concentration and the iron and aluminum contents of the water extracts from acid soils, due to moisture changes, were more or less concordant with the changes in the lime requirements and the crop-producing power of the soils.

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PLATE I Comparative growth of barley upon samples of Soil No.I, untreated and air-dried previous to planting.

PLATE II Comparative growth of barley upon samples of Soil No.II, untreated and air-dried previous to planting.

PLATES III & IV   Comparative growth of clover upon samples of Soil No.I and Soil No.II, untreated and air-dried previous to planting.

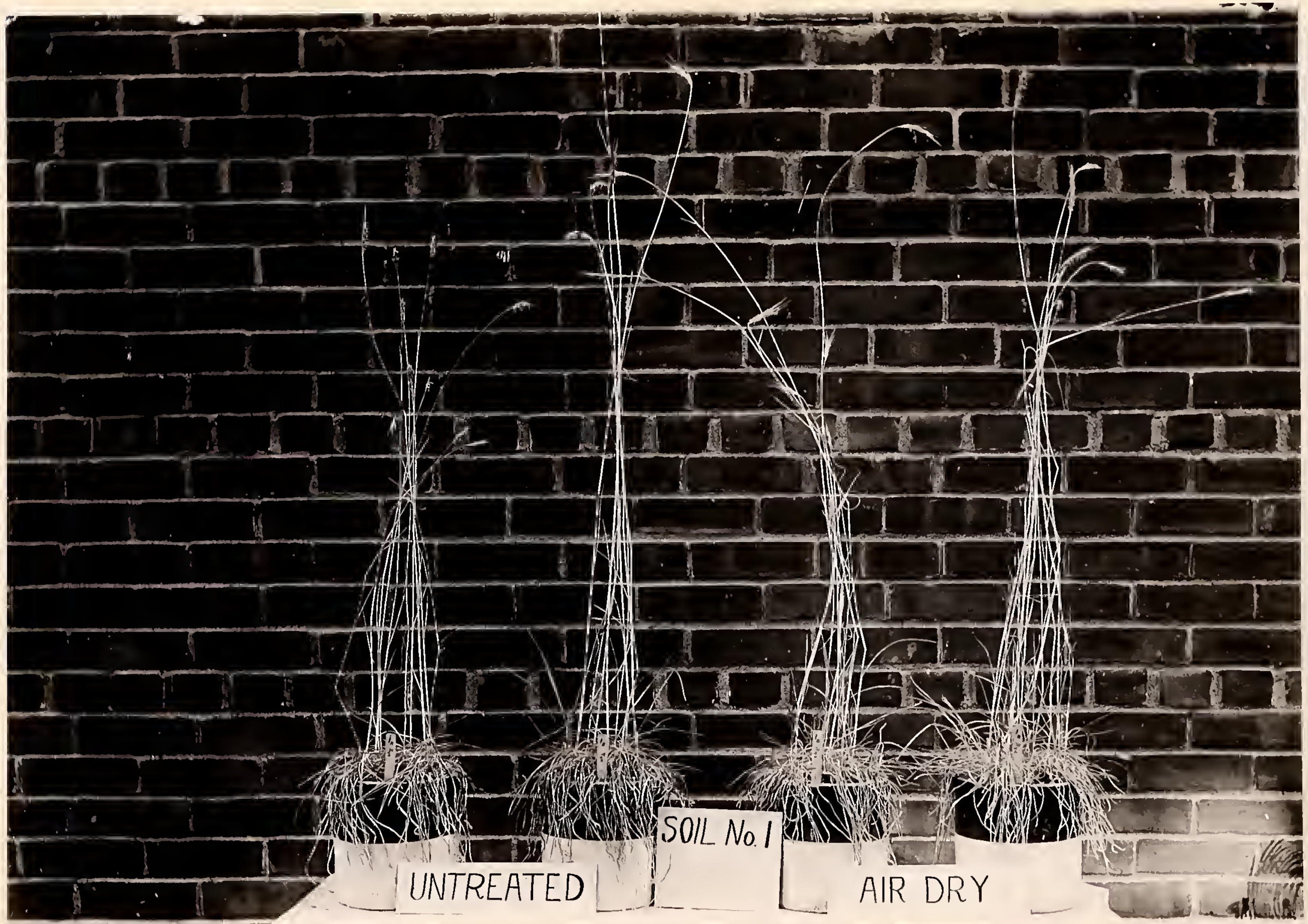


PLATE V Comparative growth of rye upon samples of Soil No.I, untreated and air-dried previous to planting.

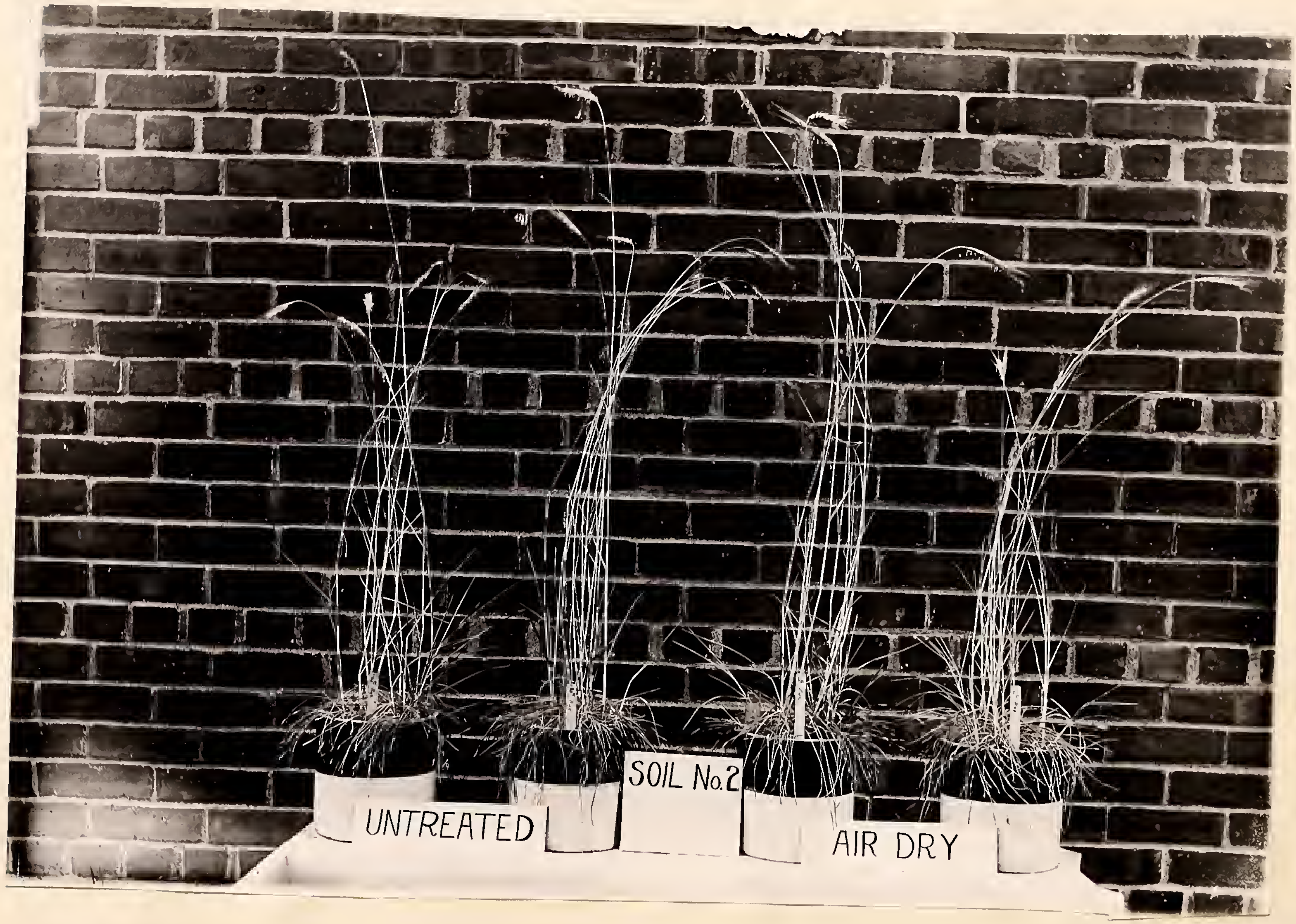


PLATE VI Comparative growth of rye upon samples of Soil No.II, untreated and air-dried previous to planting.

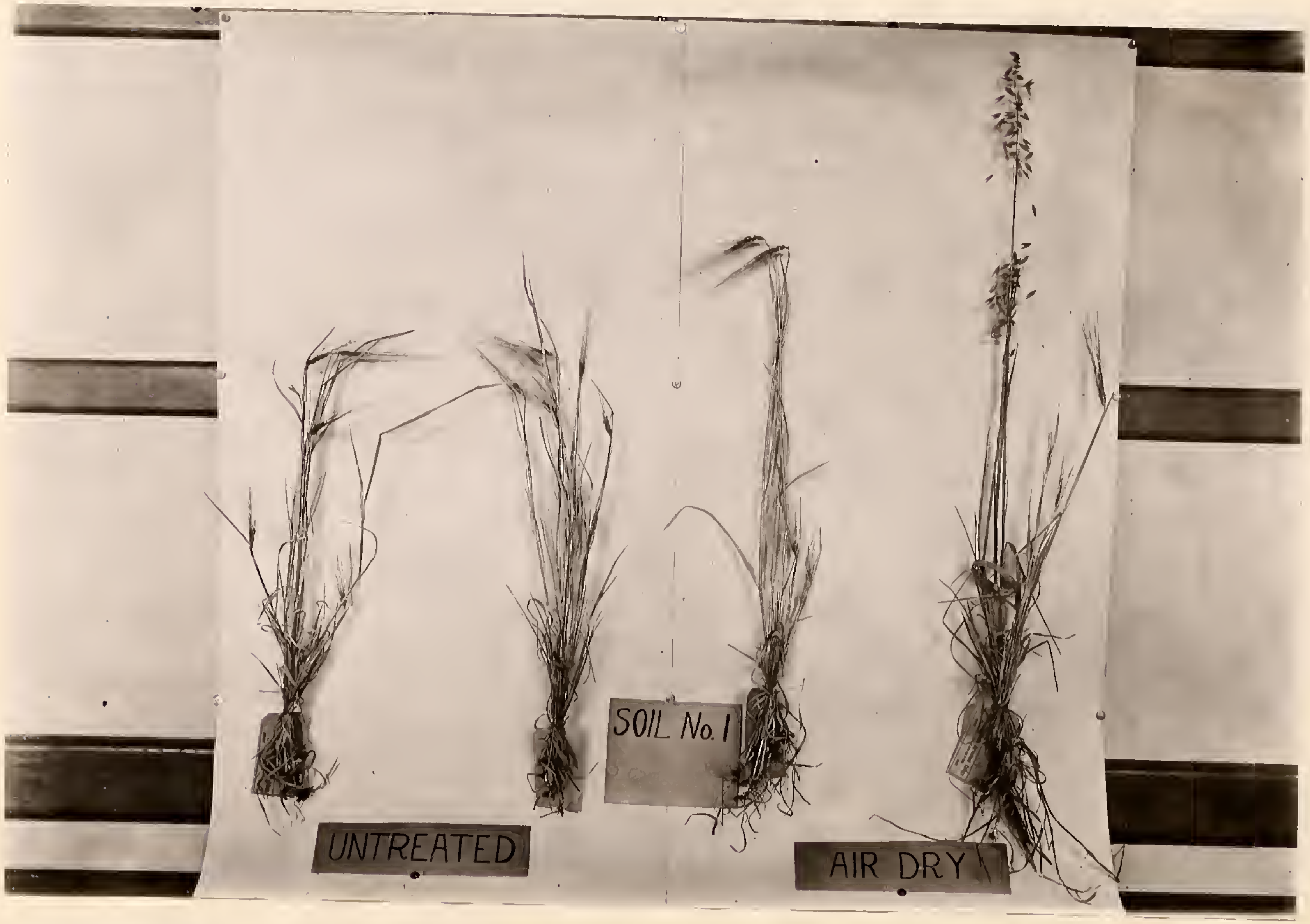


PLATE VII Comparison of the harvested crops of barley grown upon samples of Soil No.I, untreated and air-dried previous to planting.

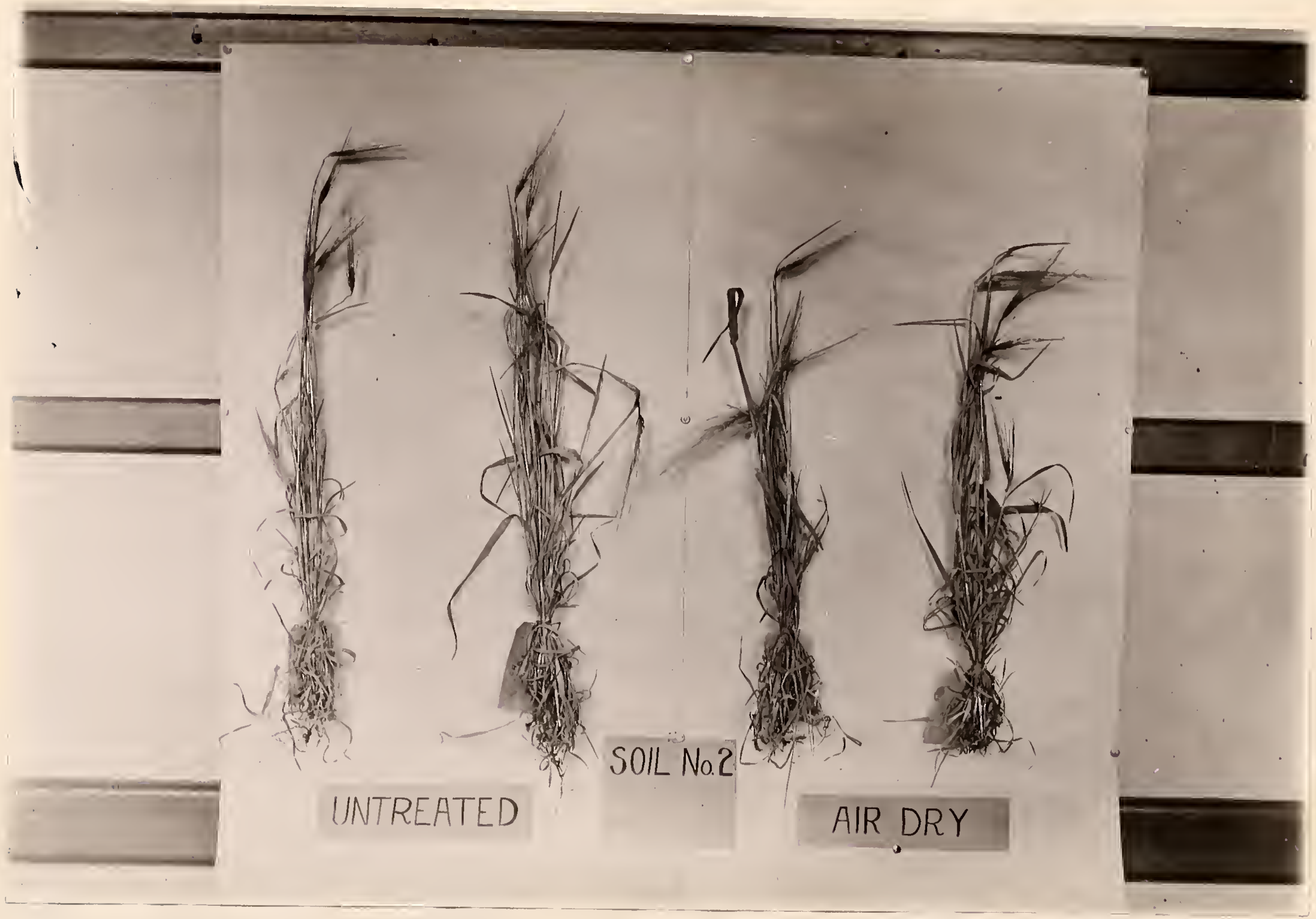
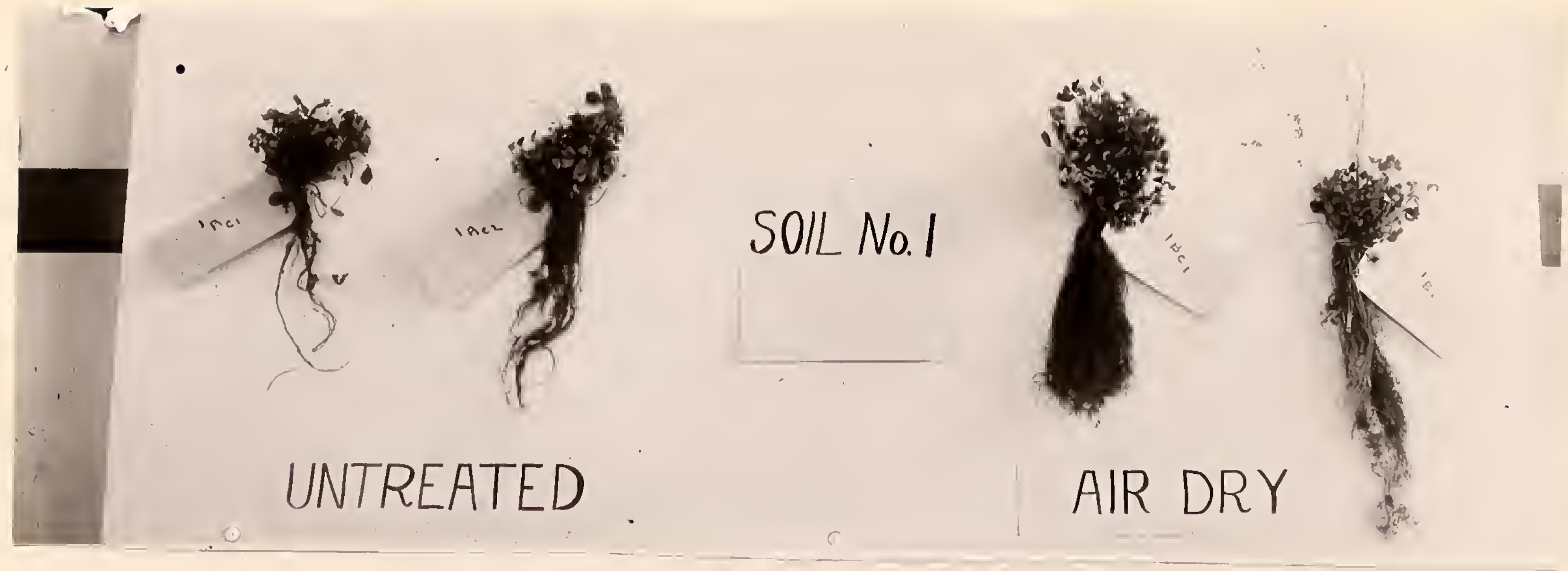


PLATE VIII   Comparison of the harvested crops of barley grown upon samples of Soil No.II, untreated and air-dried previous to planting.



PLATES IX & X   Comparison of the harvested crops of clover grown upon samples of Soil No.I and Soil No.II, untreated and air-dried previous to planting.

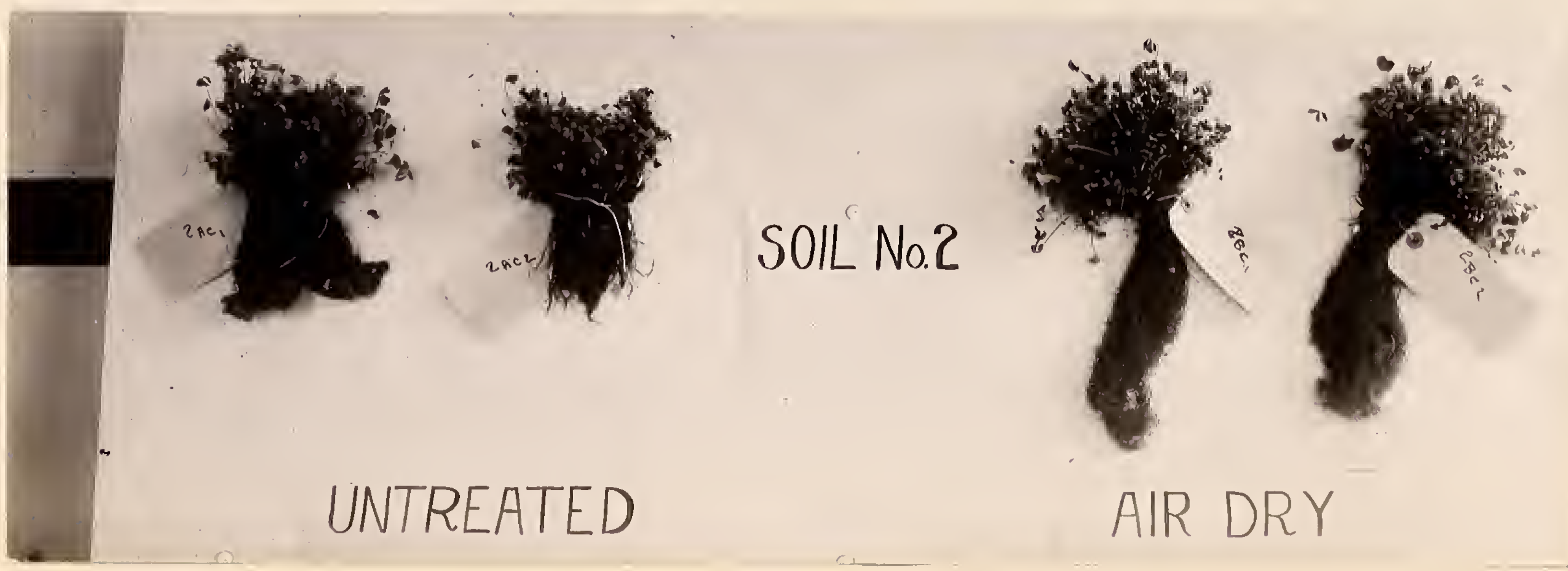


PLATE XI Comparison of the harvested crops of rye grown upon samples of Soil No.I, untreated and air-dried previous to planting.

PLATE XII Comparison of the harvested crops of rye grown upon samples of Soil No.II, untreated and air-dried previous to planting.

Mallory, Alfred Sidney (thesis)

MOISTURE CONTENT OF ACID SOILS AS A FACTOR INFLUENCING THEIR LIME REQUIREMENT

Date	Name	Address